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Volume 5



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# PHYSICAL SCIENCES

Volume 5

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Friday, January 22, 1897.

SIR FREDERICK BRAMWELL, Bart. D.C.L. LL.D. F.R.S.  
Honorary Secretary and Vice-President,  
in the Chair.

PROFESSOR DEWAR, M.A. LL.D. F.R.S. M.R.I.  
Fullerian Professor of Chemistry R.I.

*Properties of Liquid Oxygen.*

*Gaseous Absorption.*—During recent years a great deal of research has been directed to the study of what may be called the low temperature absorption spectrum of gaseous and liquid oxygen. It has been shown that gaseous oxygen gives two types of absorption spectrum, one composed of a number of well-defined groups of lines of exquisite symmetry, like the great groups A and B of the solar spectrum, the other of bands relatively broad and more or less black. The band spectrum is especially marked in gaseous oxygen under high pressure, and Janssen has shown that the intensity of absorption in different columns of gas under different pressure is identical when the length multiplied into the square of the density is the same in each case. The band that is most easily seen is one in the yellow, and, in order just to see it, 18 metres of oxygen under 11 atmospheres pressure (or 11 times the density under ordinary pressure) must be traversed by white light before it enters the spectroscope. From this result and Janssen's law just given, it follows that in order to detect the same band in a column of gaseous oxygen at atmospheric pressure, it would require to be 2178 metres long or about  $1\frac{1}{2}$  miles. The question arises what would be the length of an oxygen tube at atmospheric pressure, equivalent to the absorption of a beam passing vertically through the earth's atmosphere. This problem has been answered by Janssen, who has shown that an oxygen column 172 metres long would have a similar action. It follows at once from this result that the band in the yellow cannot be seen in the spectrum of the midday sun, as it would require a column of oxygen at least twelve times longer in order to make it visible; but that it ought to be seen provided the sun was observed near the horizon. When the sun is  $4^\circ$  above the horizon, the depth of atmosphere the rays have to penetrate is about twelve times that of the zenithal thickness. This theoretical result Janssen has confirmed by a series of observations made at sunrise in the dry air of the Desert of Sahara.

*Liquid Absorption.*—Both types of spectra are well marked in the spectrum of liquid oxygen, the only marked difference being that the

liquid absorption known as A and B of Fraunhofer appear now as bands with sharp edges on the less refrangible side, fading away gradually towards the more refrangible, which is just the opposite character to that of the gaseous absorption of the same groups. The change from the gaseous to the liquid state has not caused any material alteration in the general character of the absorption from what it was under high gaseous compression. The question may therefore naturally be put, does Janssen's law expressing the relation of absorption and density in the gaseous state extend to the liquid condition? This may be answered by calculating what thickness of the liquid at its boiling point, taken as being 800 times denser than the gas at ordinary temperatures, would be required (provided the same law held) to render visible the absorption band in the yellow. The resulting number is about 3.4 mm., and this is confirmed by laboratory experiments which show that between 3 and 4 mm. thickness of liquid oxygen at  $-183^{\circ}$  is sufficient to cause the appearance of this band. Thus it appears Janssen's law extends to the liquid condition, the square of the density still defining the intensity of the absorption. It is probable that the band spectrum has its origin either in complex molecules generated by condensation, or it may originate from encounters between molecules of the ordinary mass which become more frequent when the free path is diminished. The following table gives the results of observations (made with my colleague Prof. Liveing) in order to find the gaseous pressure required to originate definite absorption bands together with some data of liquid absorption.

Wave-Length of Band.	Atmospheric Pressure. 18-metre tube.	Atmospheric Pressure. 1.65-metre tube.	Atmospheric Pressure. 2178 metres tube.	Thickness of Liquid.
A	1	20	..	30 mm.
B	12	40		
5785 (yellow band)	11	35	1	3 to 4 mm.
6300}	20			
4700}				
5350}	30	110		
4470}				

The gaseous oxygen in the 1.65-metre tube under 85 atmospheres compression appears to be very transparent for violet and ultra-violet up to the wave-length 2745, or about the limit of the magnesium spark spectrum. When the pressure was increased to 140 atmospheres the ultra-violet absorption was complete beyond wave-length 2704. In the 18-metre tube with the oxygen under 90 atmospheres pressure, a faint absorption band appeared about L of the solar spectrum, a strong one between 3640 and 3600 wave-length, and a

diffuse band about the solar line O with complete absorption beyond P. The intensity of the absorption in the latter case was, following Janssen,  $4\frac{1}{2}$  times what it was under the highest pressure in the short tube. From this we should infer that in the liquid state medium thicknesses like a centimetre or two would be transparent to the ultra-violet, but depths of 10 to 20 cm. would become more and more opaque. Actual experiments confirm this suggestion.

Thus the passage of light through a layer of liquid 3 to 4 mm. thick is sufficient to cause visible absorption in the yellow, while it requires more than five hundred thousand times this thickness of oxygen gas at atmospheric pressure to do the same thing. Provided the density of the oxygen gas is much below that corresponding to the atmosphere, then an enormous thickness of gaseous oxygen would be required to cause any visible absorption. This may explain why such a spectrum is not shown in sunlight, quite independently of the earth's atmosphere, provided we assume that any oxygen in the solar atmosphere must have a relatively small density.

*Absorption of Liquid Air.*—If the surface of the earth was cooled to below  $-200^{\circ}$  C. then the atmosphere would liquefy, and the ocean of liquid air would form a depth of about 80 to 35 feet. The actual proportionate depth can be experimentally observed by taking a tube about 52 feet long, or about  $\frac{1}{200}$ th part of the height of the homogeneous atmosphere, and cooling one end to  $-210^{\circ}$ , when about  $\frac{3}{4}$  inch of liquid is obtained. Of this liquid air layer, about 6 to 7 feet may be taken as the equivalent of the oxygen portion. A question of considerable interest arises as to the effect of the presence of liquid nitrogen on the oxygen absorption; although nitrogen is colourless yet the dilution of the liquid oxygen in a neutral solvent has altered the concentration of the colour-absorbing medium. In order to examine into this matter Professor Liveing and the author compared the absorption of 1.9 cm. of liquid air with 0.4 cm. of liquid oxygen, or the proportionate thickness of oxygen which the layer of 1.9 cm. of liquid air contains. The light which had passed through the latter was, by means of a reflecting prism, brought into the field of view of the spectroscope at the same time with that which had passed through the liquid air. The positions of the lamps were then adjusted so that the brightness of the spectra of those parts where there were no absorption bands was equal in the two spectra. Under these circumstances it was seen that the absorption bands were very much more strongly developed by 0.4 cm. of liquid oxygen than by five times that thickness of liquid air.

Another sample of liquid air was rapidly mixed with an equal volume of liquid oxygen, and the absorption of this liquid compared as before with that of liquid oxygen. It was seen that the absorption of 2.4 cm. of the mixture was much greater than that of 0.4 cm. of liquid oxygen. The density of the liquid oxygen in the mixture was, in fact, three times that in pure liquid air, and by an extension of Janssen's law to liquid mixtures the absorption should have been

increased ninefold. The observations, so far as they go, accord with this theory. In order to examine the effect of temperature, the absorption of a thickness of 3 cm. of liquid oxygen boiling under 1 cm. pressure, or at a temperature of  $-210^{\circ}$ , was compared with a like thickness of the liquid boiling at atmospheric pressure. With the colder liquid the bands in the orange and yellow were sensibly widened, mainly on the more refrangible side; the faint band in the green was plainly darker, and the band in the blue appeared somewhat stronger. The difference between the temperatures of the two liquids was about  $27^{\circ}$ , or approaching to one-third the absolute boiling-point of oxygen. The density of oxygen at  $-210^{\circ}$  C. is not known, but in any case it is greater than that at  $-183^{\circ}$  C., and an increased absorption of about one-fourth by the cooling might be anticipated.

At the low temperature reached by the use of a hydrogen jet taken in liquid air, the latter solidifies into a hard white solid resembling avalanche snow. The solid has a pale bluish colour, showing by reflection all the absorption bands of the liquid.

The refractive power of the liquid, as determined by Prof. Liveing and the author, was given in a previous lecture.\* Later investigations resulted in the determination of the dispersive power. The refractive constant of the liquid oxygen was found to be almost identical with Mascart's value for the gas, and similarly the dispersive constant in the liquid and gas seems to be identical.

### *Magnetic Properties of Liquid Oxygen.*

The remarkable magnetic properties of liquid oxygen were described to the Royal Institution in a lecture delivered in 1892.† Professor Fleming and myself have for some time past directed our attention to the question of determining the numerical values of the magnetic permeability and magnetic susceptibility of liquid oxygen,‡ with the object of determining not only the magnitude of these physical constants, but also whether they vary with the magnetic force under which they are determined.

Although a large number of determinations have been made by many observers of the magnetic susceptibility of different liquids taken at various temperatures, difficulties of a particular kind occur in dealing with liquid oxygen. One method adopted for determining the magnetic susceptibility of a liquid is to observe the increase of mutual induction of two conducting circuits suitably placed, first in air, and then when the air is replaced by the liquid in question, the

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\* "Liquid Atmospheric Air," Proc. Roy. Inst. 1893.

† See Roy. Inst. Proc. June 15th, 1892, "On the Magnetic Properties of Liquid Oxygen." Friday evening discourse, by Professor J. Dewar, F.R.S.

‡ Proc. Roy. Soc. vol. lx. 1896, p. 283, "On the Magnetic Permeability of Liquid Oxygen and Liquid Air," by Professor J. A. Fleming, F.R.S. and Professor J. Dewar, F.R.S.

susceptibility of which is to be determined. A second method consists in determining the mechanical force acting on a known mass of the liquid when placed in a non-uniform magnetic field. Owing to the difficulty of preventing entirely the evaporation of liquid oxygen, even when contained in a good vacuum vessel, and the impossibility of sealing it up in a bulb or tube, and having regard to the effect of the low temperature of the liquid in deforming by contraction and altering the conducting power of coils of wire placed in it, it was necessary to devise some method which should be independent of the exact constancy in mass of the liquid gas operated upon, and independent also of slight changes in the form of any coils of wire which might be used in it. After many unsuccessful preliminary experiments the method which was finally adopted by Professor Fleming and myself as best complying with the conditions introduced by the peculiar nature of the substance operated upon is as follows:—

A small closed circuit transformer was constructed, the core of which could be made to consist either of liquid oxygen or else immediately changed to gaseous oxygen, having practically the same temperature. This transformer consisted of two coils, the primary coil was made of forty-seven turns of No. 12 S.W.G. wire; this wire was wound into a spiral having a rectangular shape, the rectangular turns having a length of 8 cm. and a width of 1.8 cm. This rectangular-sectioned spiral, consisting of one layer of wire of forty-seven turns, was bent round a thin brass tube, 8 cm. long and  $2\frac{1}{2}$  cm. in diameter, so that it formed a closed circular solenoid of one layer of wire. The wire was formed of high conductivity copper, doubly insulated with cotton, and each single turn or winding having a rectangular form.

The turns of covered wire closely touched each other on the inner circumference of the toroid, but on the external circumference were a little separated, thus forming apertures by which liquid could enter or leave the annular inner core.

The nature of this transformer is shown in Fig. 1.

The mean perimeter of this rectangular-sectioned endless solenoid was  $13\frac{1}{2}$  cm. and the solenoid had, therefore, very nearly 3.5 turns per cm. of mean perimeter. When immersed in liquid oxygen a coil of this kind will carry a current of 50 amperes. When a current of A amperes is sent through this coil the mean magnetising force in the axis of this solenoid is, therefore, represented by 4.375 times the current through the wire, hence it is clear that it is possible to produce in the interior of this solenoid a mean magnetising force of over 200 C.G.S. units. This primary coil had then wound over it, in two sections, about 400 or 500 turns of No. 26 silk-covered copper wire to form a secondary coil. The primary and secondary coils were separated by layers of silk ribbon. The exact number of turns was not counted, and, as will be seen from what follows, it was not necessary to know the number. The coil so constructed constituted a small

induction coil or transformer, with a closed air-core circuit, but which, when immersed in a liquid, by the penetration of the liquid into the interior of the primary coil, became changed into a closed circuit transformer, with a liquid core. The transformer so designed was capable of being placed underneath liquid oxygen contained in a large vacuum vessel, and when so placed formed a transformer of the closed circuit type, with a core of liquid oxygen. The coefficient of mutual induction of these two circuits, primary and secondary, is

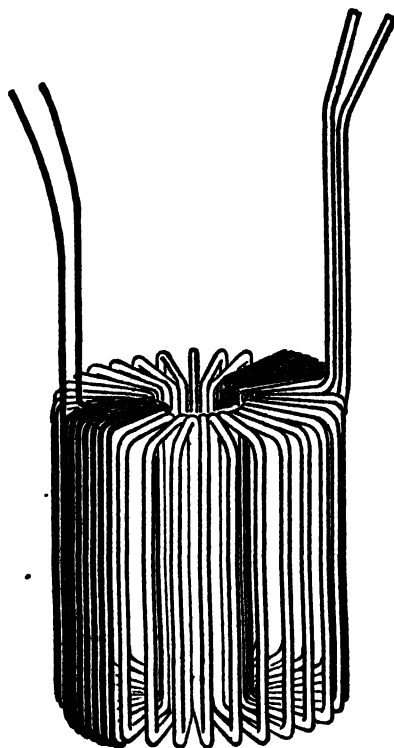


FIG. 1.—Diagram of the Closed Circuit Transformer used in Experiments.

therefore altered by immersing the transformer in liquid oxygen, but the whole of the induction produced in the interior of the primary coil is always linked with the whole of the turns of the secondary coil, and the only form-change that can be made is a small change in the mean perimeter of the primary turns due to the contraction of the coil as a whole. In experiments with this transformer the transformer was always lifted out of the liquid oxygen into the cold gaseous oxygen lying on the surface of the liquid oxygen, and

which is at the same temperature. On lifting out the transformer, the liquid oxygen drains away from the interior of the primary coil, and is replaced by gaseous oxygen of very nearly the same temperature.

The vacuum vessel used had a depth of 60 cm. outside and 53 cm. inside, and an internal diameter of 7 cm. It held 2 litres of liquid oxygen when full; but, as a matter of fact, 4 or 5 litres of liquid oxygen were poured into it in the course of the experiment.

Another induction coil was then constructed, consisting of a long cylindrical coil wound over the four layers of wire, and a secondary circuit was constructed to this coil, consisting of a certain number of turns wound round the outside of the primary coil, and a small adjusting secondary coil, consisting of a thin rod of wood wound over with very open spirals of wire. The secondary turns on the outside of the primary coil were placed in series with the turns of the thin adjusting coil, and the whole formed a secondary circuit, partly outside and partly inside the long primary cylindrical coil, the coefficient of mutual induction of this primary and secondary coil being capable of being altered by very small amounts by sliding into or out of the primary coil the small secondary coil. This last induction coil, which will be spoken of as the balancing coil, was connected up to the small transformer, as just described, as follows:—

The primary coil of the small transformer was connected in series with the primary coil of the balancing induction coil, and the two terminals of the series were connected through a reversing switch and ammeter with an electric supply circuit, so that a current of known strength could be reversed through the circuit, consisting of the two primary coils in series. The two secondary coils, the one on the transformer and the one on the balancing induction coil, were connected in opposition to one another through a sensitive ballistic galvanometer in such a manner that on reversing the primary current the galvanometer was affected by the difference between the electromotive forces set up in the two secondary coils, and a very fine adjustment could be made by moving in or out the adjusting coil of the balancing induction coil.

The arrangement of circuits is shown in Fig. 2.

For the purpose of standardising the ballistic galvanometer employed, the primary coil of the balancing induction coil could be cut out of circuit, so that the inductive effect in the ballistic galvanometer circuit was due to the primary current of the closed circuit transformer alone. A resistance box was also included in the circuit of the ballistic galvanometer. The resistance of the ballistic galvanometer was about 18 ohms, and the resistance of the whole secondary circuit 30.36 ohms. The experiment then consisted in first balancing the secondary electromotive forces in the two coils exactly against one another, then immersing the transformer in liquid oxygen, the result of which was to disturb the inductive balance, and in consequence of the magnetic permeability of the liquid oxygen core

being greater than unity, a deflection of the ballistic galvanometer was observed on reversing the same primary current. The induction through the primary circuit of the small transformer is increased in the same proportion that the permeability of the transformer core is increased by the substitution of liquid oxygen for gaseous oxygen, and hence the ballistic deflection measures at once the amount by which the magnetic permeability of the liquid oxygen is in excess over that of the air or gaseous oxygen forming the core of the transformer when the transformer is lifted out of the liquid. As a matter of fact, it was never necessary to obtain the inductive balance pre-

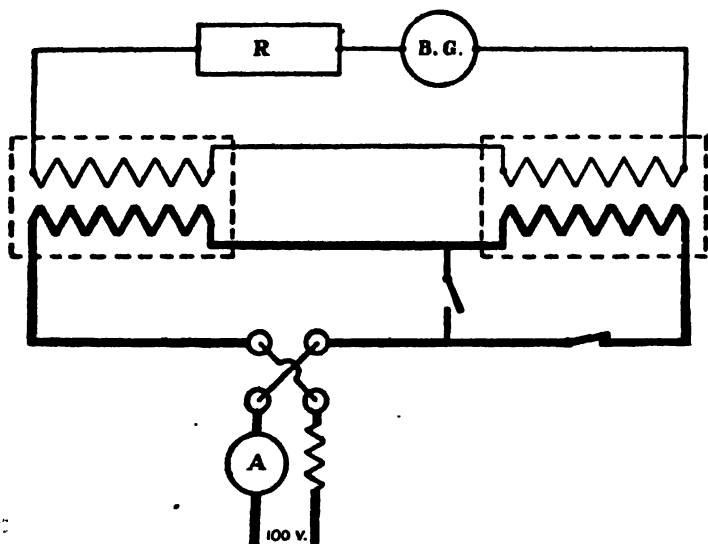


FIG. 2.—Arrangement of the Circuits of the Transformer and Induction Coil.

cisely. All that was necessary was to observe the throw of the ballistic galvanometer, first when the transformer was wholly immersed under the surface of liquid oxygen, and, secondly, when it was lifted out into the gaseous oxygen lying on the surface of the liquid, the strength of the primary current reversed being in each case the same. In order to standardise the galvanometer and to interpret the meaning of the ballistic throw, it was necessary to cut out of circuit the primary coil of the balancing induction coil, and to reverse through the primary circuit of the small transformer a known small primary current, noting at the same time the ballistic throw produced on the ballistic galvanometer, this being done when the transformer was underneath the surface of liquid oxygen. It will be seen, therefore, that this method requires no calculation of any



coefficient or mutual induction, neither does it involve any knowledge of the number of secondary turns on the transformer, nor of the resistance of the secondary circuit; all that is necessary for a successful determination of the magnetic permeability of the liquid oxygen is that the secondary circuit of the transformer should remain practically of the same temperature during the time when the throw of the ballistic galvanometer is being observed, both with the transformer underneath the liquid oxygen and out of the liquid oxygen. If then the result of reversing a current of  $A$  ampères through the two primary coils in series when the secondary coils are opposed is to give a ballistic throw  $D$ , and if the result of reversing a small current  $a$  ampères through the primary coil of the transformer alone is to produce a ballistic throw  $d$ , then, if  $\mu$  is the magnetic permeability of liquid oxygen, that of the gaseous oxygen lying above the liquid and at the same temperature being taken as unity, we have the following relation:—

$$\frac{D}{\frac{A}{a}d} = \mu - 1,$$

which determines the value of  $\mu$ .

TABLE OF RESULTS OF OBSERVATIONS ON THE MAGNETIC PERMEABILITY OF LIQUID OXYGEN.

$A$ = primary current, in ampères, passing through primaries of the transformer and balancing coil.	Corresponding mean magnetising force in C.G.S. units in primary circuit of transformer.	Total ballistic throw which would be produced if primary current of $A$ ampères were reversed through primary of transformer alone $= \frac{A}{a}d$ .	Ballistic throw of galvanometer resulting from immersion of the transformer in liquid oxygen. Transformer and balancing induction coil being opposed $= D$ .	$\mu$ = permeability, calculated from $\mu - 1 = \frac{D}{\frac{A}{a}d}$ .
8.037	35.2	1,734	4.33	1.00250
28.13	123.0	6,068	14.9	1.00246
37.8	165.4	8,153	21.18	1.00260
36.8	161.0	7,938	23.57	1.00297
50.5	220.9	10,894	32.98	1.00304

The values of the permeability given in the foregoing table are not all of equal weight.

The value, viz. 1.00287, found by Professor Fleming and the author for the magnetic permeability of liquid oxygen, shows that the magnetic susceptibility ( $k$ ) per unit of volume is  $228/10^6$ . It is interesting to compare this value with the value obtained by

Mr. Townsend for an aqueous solution of ferric chloride, and which he states can be calculated by the equation

$$10^6 k = 91.6 w - 0.77,$$

where  $w$  is the weight of salt in grams per cubic centimetre, and  $k$  the magnetic susceptibility. Even in a saturated solution,  $w$  cannot exceed 0.6, hence, from the above equation, we find the value of the magnetic susceptibility of a saturated solution of one of the most paramagnetic iron salts, viz. ferric chloride, is  $54/10^6$  for magnetic forces between 1 and 9. This agrees fairly well with other determinations of the same constant. On the other hand, the magnetic susceptibility of liquid oxygen for the same volume is  $228/10^6$ , or more than *four times as great*. The unique position of liquid oxygen in respect of its magnetic susceptibility is thus strikingly shown. It is, however, interesting to note that its permeability lies far below that of certain solid iron alloys generally called non-magnetic.

In the course of these investigations valuable assistance has been given by Mr. Robert Lennox and Mr. J. W. Heath.

[J. D.]

Friday, January 29, 1897.

SIR JAMES CRICHTON-BROWNE, M.D. LL.D. F.R.S. Treasurer  
and Vice-President, in the Chair.

PROFESSOR JAGADIS CHUNDER BOSE, M.A. D.Sc.  
Professor of Physics in the Presidency College, Calcutta.

*Electro-Magnetic Radiation and the Polarisation of the Electric Ray.*

THE great work of Hertz in verifying the anticipations of Maxwell has been followed in this country by many important investigations on Electric Waves. The Royal Institution witnessed the repetition of some of the brilliant experiments of Professors Fitzgerald and Lodge. My interest in the subject, and inspiration for work, are to a great extent derived from the memorable addresses delivered in this hall, and I am glad to have an opportunity to lay before you, at this very same place, an account of some work I have been able to carry out.

As the subject of ether waves produced by periodic electric disturbances is to be dealt with in this lecture, a few models exhibiting the production of material waves by periodic mechanical disturbances may be of interest. A pendulum swings backwards and forwards at regular intervals of time; so does an elastic spring when bent and suddenly released. These periodic strokes produce waves in the surrounding medium; the aerial waves striking the ear may, under certain conditions, produce the sensation of sound. The necessary condition for audibility is, that the frequency of vibration should lie within certain limits.

As the air is invisible, we cannot see the waves that are produced. Here is a model in which the medium is thrown into visible waves by the action of periodic disturbances. The beaded string representing the medium is connected at its lower end with a revolving electric motor. The rotation of the motor is periodic; observe how the periodic rotation throws the string into wave forms; how these waves carry energy from the source to a distant place; how a suitable receiver, a bell for example, is made to respond. I now produce quicker rotation by sending a stronger current through the motor; the frequency or pitch is raised, and the waves formed are seen to become shorter. By means of the attached counter, the different frequencies are determined.

Here is a second model, a spiral spring, attached to which is a thin string. As the string is pulled, the spring is strained more and more, till the thread suddenly breaks. The spring, suddenly released, is seen to oscillate up and down. Electric vibration is produced in

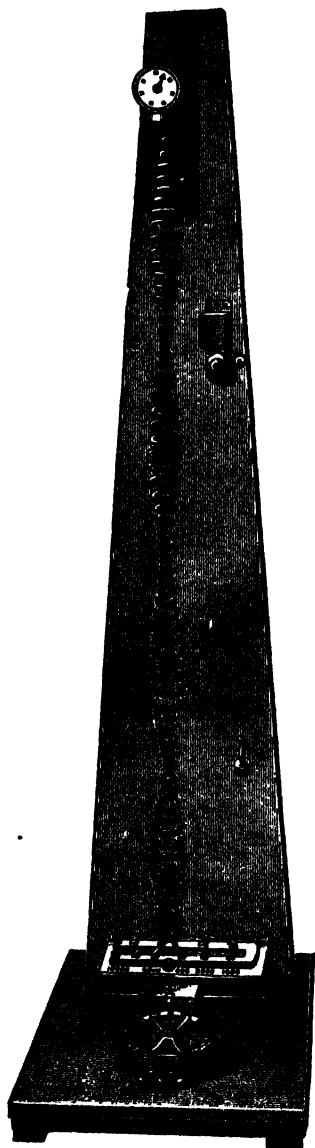


FIG. 1.—Mechanical Wave Apparatus.  
(The current regulating the speed of rotation is varied by an interposed rheostat. The counter is at the top.)

a somewhat similar way. If two metallic spheres be strongly charged with opposite electrifications, the medium is electrically strained, and when this strain is suddenly removed by a discharge, waves are produced in the medium. The discharge is oscillatory, consisting of backward and forward rushes of electricity; positive electricity flowing now in one direction, and immediately afterwards in an opposite direction. These rapid alternate flows, giving rise to ether vibration, may be illustrated by a modification of the well-known Cartesian diver experiment. By means of a bulb and connecting tube, alternate compression and rarefaction may be produced in the cylinder, attended with alternate rushes of air-currents through the connecting tube. These give rise to oscillation of the immersed ball.

By oscillatory electric discharge, waves are produced in the ether. To produce oscillatory discharge, Hertz used plates or rods with sparking balls at the ends. He found that the sparks ceased to be oscillatory as soon as the surface of the sparking balls got roughened; there was then a leak of electricity, and no sudden discharge. The balls had to be taken out every now and then for repolishing, and the process was tedious in the extreme. Prof. Lodge made the important discovery that if two side balls were made to spark into an interposed third ball, the oscillatory nature of the discharge was not affected

to so great an extent by a change in the nature of the surface. But even here the disintegration of the sparking surface produced by a torrent of sparks soon puts an end to oscillation. I found this difficulty removed to a great extent by making the balls of platinum, which resists the disintegrating action. I also found that it was not at all necessary to have a series of useless sparks, which ultimately spoils the efficiency of the radiator and makes its action uncertain. A flash of radiation for an experiment is obtained from a single spark, and for a series of experiments one does not require more than fifty or a hundred sparks, which do not in any way affect the radiator. As an electric generator I use a small and modified form of Ruhmkorff's coil, actuated by a single storage cell. A spark is produced by a short contact and subsequent break of a tapping key. With these modifications one of the most troublesome sources of uncertainty is removed. The coil and the cell are inclosed in a small double-walled metallic box, with a tube for the passage of the electric beam. The magnetic variation due to the make and break of the primary of the Ruhmkorff's coil, disturbs the receiver. This difficulty is removed by making the inner box of soft iron, which acts as a magnetic screen.

A few words may here be said about the necessary conditions to be kept in view in making an electric wave apparatus an instrument of precision. If one merely wishes to produce response in a receiver at a distance, the more energetic the vibration is, the more likely it is to overcome obstacles. The waves may with advantage be of large size, as they possess very great penetrative power. The surface or the depth of the sensitive layer in the receiver may be extended, for if one part of it does not respond another part will. But for experimental investigations the conditions to be fulfilled are quite different. Too great an intensity of radiation makes it almost impossible to prevent the disturbance due to stray radiation. As the waves are invisible, it is difficult to know through what unguarded points they are escaping. They may be reflected from the walls of the room or the person of the experimenter, and falling on the receiver disturb it.

The radiation falling on any portion of the receiving circuit—the leading wires or the galvanometer—disturbs the delicate receiver. It is extremely difficult to shield the receiving circuit from the disturbing action of stray radiation. These difficulties were, however, successfully removed by the use of short electric waves. With these, it is not at all necessary to take special precautions to shield either the galvanometer or the leading wires, the sensitive layer in the receiver alone being affected by the radiation. The bare leading wires may be exposed in close proximity to the source of radiation, and yet no disturbance is produced.

For experimental investigations it is also necessary to have a narrow pencil of electric radiation, and this is very difficult to obtain, unless waves of very short length are used. With large waves diverging in all directions and curling round corners, all attempt at accurate work is futile. For angular measurements it is necessary to direct

the electric beam in the given direction along narrow tubes, and receive it in another tube in which is placed the receiver. The waves experience great difficulty in passing through narrow apertures, and there are other troubles from the interference of direct and reflected waves. These difficulties were ultimately overcome by making suitable radiators emitting very short waves; the three radiators here exhibited, give rise to waves which are approximately  $\frac{1}{4}$  inch,  $\frac{1}{2}$  inch and 1 inch in length. The intensity of emitted radiation is moderately strong, and this is an advantage in many cases. It sometimes becomes necessary to have a greater intensity without the attendant trouble inseparable from too long waves. I have been able to secure this by making a new radiator, where the oscillatory discharge takes place between two circular plates and an interposed platinum ball. The sparking takes place at right angles to the circular plates. The intensity of radiation is by this expedient very greatly increased. The parallel pencil of electric radiation, used in many of the experiments to be described below, is only about half an inch in diameter. The production of such a narrow pencil became absolutely necessary for a certain class of investigations. Merely qualitative results for reflection or refraction may no doubt be obtained with gigantic mirrors or prisms, but when we come to study the phenomena of polarisation as exhibited by crystals, Nature imposes a limit, and this limitation of the size of the crystals has to be accepted in conducting any investigation on their polarising properties.

The greatest drawback, however, in conducting experimental investigations with electric radiation arises from the difficulty of constructing a satisfactory receiver for detecting these waves. For this purpose I at first used the original form of coherer made of metallic filings as devised by Professor Lodge. It is a very delicate detector for electric radiation, but unfortunately I found its indications often to be extremely capricious.

The conditions for a satisfactory receiver are the following:—

- (1) Its indications should always be reliable.
- (2) Its sensitiveness should remain fairly uniform during the experiment.
- (3) The sensibility should be capable of variation, to suit different experiments.
- (4) The receiver should be of small size, and preferably linear, to enable angular measurements to be taken with accuracy.

These conditions seemed at first almost impossible to be attained. The coherer sometimes would be so abnormally sensitive that it would react without any apparent cause. At other times, when acting in an admirable manner, the sensitiveness would suddenly disappear at the most tantalising moment. It was a most dreary experience when the radiator and the receiver failed by turns, and it was impossible to find out which was really at fault.

From a series of experiments carried out to find the causes which may affect prejudicially the action of the receiver, I was led to sup-

pose that the uncertainty in the response of the receiver is probably due to the following:—

(1) Some of the particles of the coherer might be too loosely applied against each other, whereas others, on the contrary, might be jammed together, preventing proper response.

(2) The loss of sensibility might also be due to the fatigue produced on the contact surfaces by the prolonged action of radiation.

(3) As the radiation was almost entirely absorbed by the outermost layer, the inner mass, which acted as a short circuit, was not necessary.

For these reasons I modified the receiver into a spiral-spring form. Fine metallic wires (generally steel, occasionally others, or a combination of different metals) were wound in narrow spirals and laid in a single layer on a groove cut in ebonite, so that the spirals could roll on a smooth surface. The ridges of the contiguous spirals made numerous and well-defined contacts, about one thousand in number. The useless conducting mass was thus abolished, and the resistance of the receiving circuit almost entirely concentrated at the sensitive contact surface exposed to radiation. If any change of resistance, however slight, took place at the sensitive layers, the galvanometer in circuit would show strong indications. The pressure throughout the mass was made uniform as each spring transmitted the pressure to the next. When the contact surfaces had too long been acted on, fresh surfaces could easily be brought into contact by the simultaneous rolling of all the spirals.

The sensibility of the receiver to a given radiation, I found, depends (1) on the pressure to which the spirals are subjected, and (2) on the E.M.F. acting on the circuit. The pressure on the spirals may be adjusted, as will be described later on, by means of a fine screw. The E.M.F. is varied by a potentiometer-slide arrangement. This is a matter of great importance, as I often found a receiver, otherwise in good condition, failing to respond when the E.M.F. varied slightly from the proper value. The receiver, when subjected to radiation, undergoes exhaustion. The sensibility can, however, be maintained fairly uniform by slightly varying the E.M.F. to keep pace with the fatigue produced.

The receiving circuit thus consists of a spiral-spring coherer, in series with a voltaic cell and a dead-beat galvanometer. The receiver is made by cutting a narrow groove in a rectangular piece of ebonite, and filling the groove with bits of coiled spirals arranged side by side in a single layer. The spirals are prevented from falling by a glass slide in front. They are placed between two pieces of brass, of which the upper one is sliding and the lower one fixed. These two pieces are in connection with two projecting metallic rods, which serve as electrodes. An electric current enters along the breadth of the top spiral and leaves by the lowest spiral, having to traverse the intermediate spirals along the numerous points of contact. When electric radiation is absorbed by the sensitive sur-

face, there is a sudden diminution of the resistance, and the galvanometer spot is violently deflected.

By means of a very fine screw the upper sliding piece can be gently pushed in or out. In this way the spirals may be very gradually compressed, and the resistance of the receiver diminished. The galvanometer spot can thus easily be brought to any convenient position on the scale. When electric radiation falls on the sensitive surface the spot is deflected. By a slight unscrewing the resistance is increased, and the spot made to return to its old position. The receiver is thus re-sensitised for the next experiment.

The receiver thus constructed is perfectly reliable; the sensibility can be widely varied to suit different experiments, and this sensibility maintained fairly uniform. When necessary, the sensitiveness can be exalted to almost any extent, and it is thus possible to carry out some of the most delicate experiments (specially on polarisation) with certainty.

The main difficulties being thus removed, I attempted to construct a complete electric wave apparatus, which would be portable, with which all the experiments on electric radiation could be carried out with almost as great an ease and certainty as corresponding experiments on light, and which would enable one to obtain even quantitative results with fair accuracy.

The complete apparatus is here exhibited; all its different parts, including the galvanometer, and all the accessories for reflection, refraction, polarisation, and other experiments, are contained in a small case only 2 feet in length, 1 foot in height and 1 foot in breadth. The apparatus can be set up in a few minutes, the various adjustments requiring only a short time.

The radiating apparatus is 6 by 5 by 3 inches, the size of a small lantern. It contains the coil and a small storage cell; the radiator tube is closed with a thin plate of ebonite to prevent deposit of dust on the radiator. One charge of the cell stores enough energy for experiments to be carried out for nearly a month. It is always ready for use and requires very little attention. A flash of radiation for an experiment is produced by a single tap and break of the interrupting key.

The radiating apparatus and the receiver are mounted on stands sliding in an optical bench. Experiments are carried out with divergent or parallel beams of electric radiation. To obtain a parallel beam, a lens of sulphur or glass is mounted in a tube. Suitable lenses can be constructed from the accurate determination, which I have been able to make, of the indices of refraction of various substances for the electric ray, by a method which will be described later on. This lens-tube fits on the radiator-tube, and is stopped by a guide when the oscillatory spark is at the principal focus of the lens. The radiator-tube is further provided with a series of diaphragms by which the amount of radiation may be varied.

For experiments requiring angular measurement, a spectrometer-



circle is mounted on one of the sliding stands. The spectrometer carries a circular platform, on which the various reflectors, refractors, &c., are placed. The platform carries an index, and can rotate independently of the circle on which it is mounted. The receiver is carried on a radial arm (provided with an index), and points to the centre of the circle. An observing telescope may also be used with a glass objective, and a linear receiver at the focus.

I shall now exhibit some of the principal experiments on electric radiation.

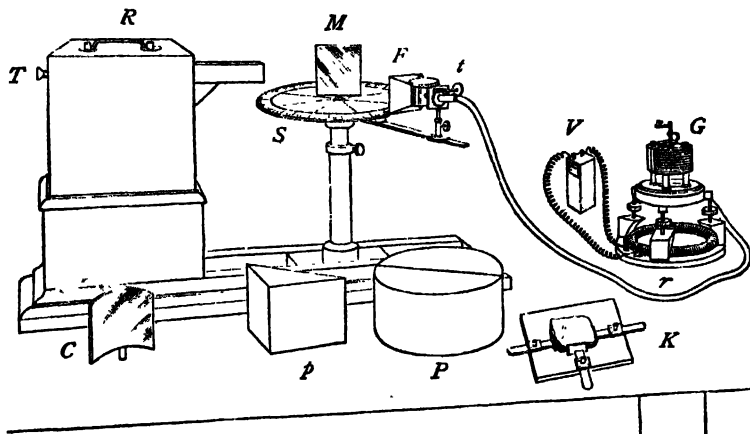


FIG. 2.—Arrangement of the Apparatus. One-sixth nat. size.

R, radiator; T, tapping key; S, spectrometer-circle; M, plane mirror; C, cylindrical mirror; p, totally reflecting prism; P, semi-cylinders; K, crystal-holder; F, collecting funnel attached to the spiral spring receiver; t, tangent screw, by which the receiver is rotated; V, voltaic cell; r, circular rheostat; G, galvanometer.

### *Selective Absorption.*

I arrange the radiation apparatus so that a parallel beam of electric radiation proceeding from the lantern falls on the receiver placed opposite; the receiver responds energetically, the light-spot from the galvanometer being swept violently across the screen. I now interpose various substances to find out which of them allow the radiation to pass through and which do not. A piece of brick, or a block of pitch, is thus seen to be quite transparent, whereas a thick stratum of water is almost opaque. A substance is said to be coloured when it allows light of one kind to pass through, but absorbs light of a different kind. A block of pitch is opaque to visible light, but transparent to electric radiation; whereas water, which is transparent to light, is opaque to electric radiation. These substances exhibit selective absorption, and are therefore coloured.

There is an interesting speculation in reference to the possibility of the sun emitting electric radiation. No such radiation has yet been detected in sunlight. It may be that the electric rays are absorbed by the solar or the terrestrial atmosphere. As regards the latter supposition, the experiment which I am able to exhibit on the transparency of liquid air may be of interest. Professor Dewar has kindly lent me this large bulb full of liquid air, which is equivalent to a great thickness of ordinary air. This thick stratum allows the radiation to pass through with the greatest facility, proving the high transparency of the liquid air.

### *Verification of the Laws of Reflection.*

A small plane metallic mirror is mounted on the platform of the spectrometer-circle. The receiver is mounted on a radial arm. The law of reflection is easily verified in the usual way. The second mirror, which is curved, forms an invisible image of the source of radiation. As I slowly rotate the cylindrical mirror, the invisible image moves through space; now it falls on the receiver, and there is a strong response produced in the receiver.

### *Refraction.*

Deviation of the electric ray by a prism may be shown by a prism made of sulphur or ebonite. More interesting is the phenomenon of total reflection. A pair of totally-reflecting prisms may be obtained by cutting a cube of glass, which may be an ordinary paper-weight, across a diagonal. The critical angle of a specimen of glass I found to be  $29^{\circ}$ , and a right-angled isosceles prism of this material produces total reflection in a very efficient manner. When the receiver is placed opposite the radiator, and the prism interposed with one of its faces perpendicular to the electric beam, there is not the slightest action on the receiver. On turning the receiver through  $90^{\circ}$ , the receiver responds to the totally-reflected ray.

Opacity due to multiple refraction and reflection, analogous to the opacity of powdered glass to light, is shown by filling a long trough with irregularly-shaped pieces of pitch, and interposing it between the radiator and the receiver. The electric ray is unable to pass through the heterogeneous media, owing to the multiplicity of refractions and reflections, and the receiver remains unaffected. But on restoring partial homogeneity by pouring in kerosene, which has about the same refractive index as pitch, the radiation is easily transmitted.

### *Determination of the Index of Refraction.*

Accurate determination of the indices of refraction becomes important when lenses have to be constructed for rendering the electric beam parallel. The index for electric radiation is often very different

from the optical index, and the focal distance of a glass lens for light gives no clue to its focal distance for electric radiation. I found, for example, the index of refraction of a specimen of glass to be 2.04, whereas the index of the same specimen for sodium light is only 1.53.

There are again many substances, like the various rocks, wood, coal-tar, and others, whose indices cannot be determined owing to their opacity to light. These substances are, however, transparent to electric radiation, and it is therefore possible to determine their electric indices. For the determination of the index, the prism-method is not very suitable. I found the following method, of which I shall exhibit the optical counterpart, to yield good results. When light passes from a dense to a light medium, then, at a certain critical angle, the light is totally reflected, and from the critical angle the index can be determined. I have here a cylindrical trough filled with water. Two glass plates inclosing a parallel air-film are suspended vertically across the diameter of the cylinder, dividing the cylinder into two halves. The cylinder, mounted on a graduated

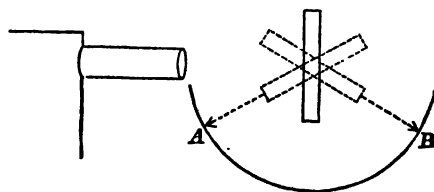


FIG. 3.

(The dotted lines show the two positions of the air-film for total reflection.)

circle, is adjusted in front of an illuminated slit, an image of the slit being cast by the water-cylinder on the screen. The divergent beam from the slit, rendered nearly parallel by the first half of the cylinder, is incident on the air-film, and is then focussed by the second half of the cylinder. As the cylinder is slowly rotated, the angle of incidence at the air-film is gradually increased, but the image on the screen remains fixed. On continuing the rotation you observe the almost sudden extinction of the image. I say almost, because the light is not monochromatic, and the different components of white light undergo total reflection in succession. Just before total extinction the image you observe is reddish in colour, the violet and the blue lights being already reflected. On continuing the rotation the image is completely extinguished. Rotation of the cylinder in an opposite direction gives another reading for total reflection, and the difference of the two readings is evidently equal to twice the critical angle.

In a similar way I have been able to determine the indices of refraction of various substances, both solid and liquid, for electric radiation. In the case of solids, two semi-cylinders, separated by a

suitable parallel air-space, are placed on the spectrometer-circle, the receiver being placed opposite the radiator. The trouble of following the deviated ray is thus obviated. The index of refraction of glass I found to be 2.04; that of commercial sulphur is 1.73.

### *Double Refraction and Polarisation.*

I now proceed to demonstrate some of the principal phenomena of polarisation, especially in reference to the polarisation produced by crystals and other substances, and by dielectrics when subjected to molecular stress due to pressure or unequal heating.

As the wave-length of electric radiation is many thousand times the wave-length of light, there is a misgiving as to whether it would

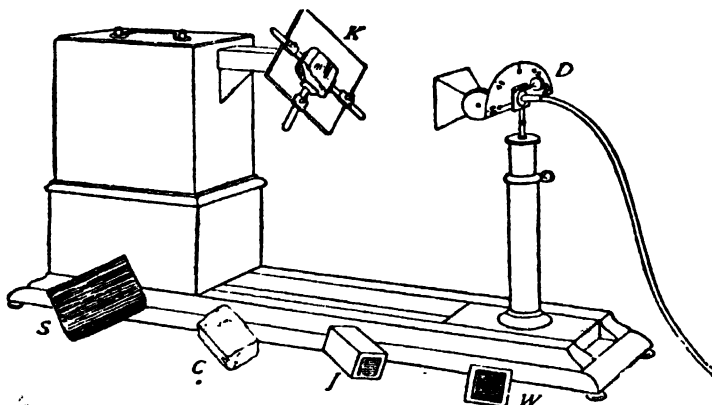
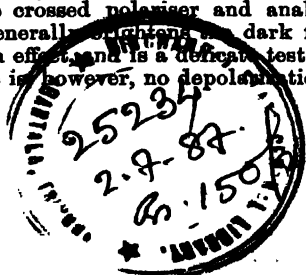


FIG. 4.—Polarisation Apparatus.

K, crystal-holder; S, a piece of stratified rock; C, a crystal; J, jute polariser; W, wire-grating polariser; D, vertical graduated disc, by which the rotation is measured.

be possible to exhibit polarisation effects with crystals of ordinary size. I hope to be able to demonstrate that such a misgiving is groundless.

A beam of ordinary light incident on a crystal of Iceland spar is generally bifurcated after transmission, and the two emergent beams are found polarised in planes at right angles to each other. The usual optical method of detecting the bi-refringent action of crystal, is to interpose it between the crossed polariser and analyser. The interposition of the crystal generally brightens a dark field. This is the so-called depolarisation effect, and is a delicate test for double-refracting substances. There is, however, no depolarisation when the



principal plane of the crystal coincides with the polarisation planes of either the polariser or the analyser. The field also remains dark when the optic axis of the crystal is parallel to the incident ray.

A similar method is adopted for experimenting with polarised electric radiation.

The spectrometer-circle is removed from the optical bench, and an ordinary stand for mounting the receiver substituted. By fitting the lens-tube, the electric beam is made parallel. At the end of the tube may be fixed either the grating polariser or the jute or serpentine polarisers, to be subsequently described.

The receiver fitted with the analyser is adjusted by a tangent screw, the rotation of the analyser being measured by means of an index and a graduated vertical disc.

The polarising gratings may be made, according to Hertz, by winding copper wires, parallel, round square frames. The polarisation apparatus is, however, so extremely delicate, that unless all the wires are strictly parallel, and the gratings *exactly* crossed, there is always a resolved component of radiation which acts on the sensitive receiver. It is a very difficult and tedious operation to cross the gratings. I have found it to be a better plan to take two thick-square plates of copper of the same size, and, placing one over the other, cut a series of slits (which stop short of the edges) parallel to one of the edges. One of these square pieces serves as a polariser, and the other as an analyser. When the two square pieces are adjusted, face to face, with coincident edges, the gratings must either be parallel or exactly crossed. Such accurate adjustments make it possible to carry out some of the most delicate experiments.

The radiator-tube, with the lens and the attached polariser, is capable of rotation. The emergent beam may thus be polarised in a vertical or a horizontal plane. The analyser fitted on to the receiver may also be rotated. The gratings may thus be adjusted in two positions.

- (1) Parallel position.
- (2) Crossed position.

In the first position the radiation is transmitted through both the gratings, falls on the sensitive surface, and the galvanometer responds. The field is then said to be bright. In the second position the radiation is extinguished by the crossed gratings, the galvanometer remains unaffected, and the field is said to be dark. But in interposing a double-refracting substance in certain positions between the crossed gratings, the field is partially restored, and the galvanometer-spot sweeps across the scale.

I have now the analyser and the polariser exactly crossed, and there is not the slightest action on the receiver. Observe the great sensitiveness of the arrangement; I turn the polariser very slightly from the crossed position, and the galvanometer-spot is violently deflected.

I now readjust the gratings in a crossed position. I have in my hand a large block of the crystal beryl; it is perfectly opaque to light. I now hold the crystal with its principal plane inclined at  $45^\circ$  between the crossed gratings, and the galvanometer-spot, hitherto quiescent, sweeps across the scale. It is very curious to observe the restoration of the extinguished field of electric radiation, itself invisible, by the interposition of what appears to the eye to be a perfectly opaque block of crystal. If the crystal is slowly rotated, there is no action on the receiver when the principal plane of the crystal is parallel to either the polariser or the analyser. Thus, during one complete rotation there are four positions of the crystal when no depolarisation effect is produced.

Rotation of the crystal, when held with its optic axis parallel to the incident ray, produces no action. The field remains dark.

Here is another large crystal, idocrase, belonging to the orthorhombic system, which shows the same action. It is not at all necessary to have large crystals; a piece of calc-spar, taken out of an optical instrument, will polarise the electric ray. But the effect produced by the crystal epidote seems extraordinary. I have here a piece with a thickness of only  $\cdot 7$  cm.—a fraction of the wave-length of the electric radiation—and yet observe how strong is its depolarising effect.

I subjoin a representative list of crystals belonging to the different systems, which would be found to produce double refraction of the electric ray.

*Tetragonal System.*—Idocrase, scapolite.

*Orthorhombic System.*—Barytes, celestine, cryolite, andalusite, hypersthene.

*Hexagonal System.*—Calcite, apatite, quartz, beryl, tourmaline.

*Monoclinic System.*—Selenite, orthoclase, epidote.

*Triclinic System.*—Labradorite, microcline, amblygonite.

### *Double Refraction produced by a Strained Dielectric.*

*Effect due to Pressure.*—A piece of glass, when strongly compressed, becomes double refracting for light. An analogous experiment may be shown with electric radiation. Instead of producing pressure artificially, it seemed to me that stratified rocks, which, from the nature of their formation, were subjected to great pressure, would serve well for my experiment. Here is a piece of slate about an inch in thickness. I interpose this piece with the plane of stratification inclined at  $45^\circ$ , and the spot of light flies off the scale. I now carefully rotate the piece of slate; there is no depolarisation effect when the plane of stratification is parallel to either the polariser or the analyser. Thus the existence of strain inside an opaque mass can easily be detected, and what is more, the directions of maximum and minimum pressures can be determined with great exactitude.

*Effect due to Strains in Cooling.*—An effect similar to that pro-

duced by unannealed glass may be shown by this piece of solid paraffin, which was cast in a mould, and chilled unequally by a freezing mixture. One of these blocks was cast two years ago, and it has still retained its unannealed property. This effect may even be shown without any special preparation. Pieces of glass or ebonite, too, are often found sufficiently strained to exhibit double refraction.

### *Phenomena of Double Absorption.*

Being desirous of making a crystal polariser, I naturally turned to tourmaline, but was disappointed to find it utterly unsuitable as a polariser. There is a difference in transparency in directions parallel and perpendicular to the length, but even a considerable thickness of the crystal does not completely absorb one of the two rays. Because visible light is polarised by absorption by tourmaline, it does not follow that all kinds of radiation would be so polarised. The failure of tourmaline to polarise the Röntgen rays is therefore not unexpected, supposing such rays to be capable of polarisation.

It was a long time before I could discover crystals which acted as electric tourmalines. In the meanwhile I found many natural substances which produced polarisation by selective unilateral absorption. For example, I found locks of human hair to polarise the electric ray. I have here two bundles of hair; I interpose one at  $45^\circ$ , and you observe the depolarisation effect. The darker specimen seems to be the more efficient. Turning to other substances more easily accessible, I found vegetable fibres to be good polarisers. Among these may be mentioned the fibres of aloes (*Agave*), rhea (*Boehmeria nivea*), pine-apple (*Ananas sativus*), plantain (*Musa paradisiaca*). Common jute (*Corchorus capsularis*) exhibits the property of polarisation in a very marked degree. I cut fibres of this material about 3 cm. in length, and built with them a cell with all the fibres parallel. I subjected this cell to a strong pressure under a press. I thus obtained a compact cell 3 cm. by 3 cm. in area, and 5 cm. in thickness. This was mounted in a metallic case, with two openings 2 cm. by 2 cm. on opposite sides for the passage of radiation. This cell absorbs vibrations parallel to the length of the fibres, and transmits those perpendicular to the length. Two such cells could thus be used, one as a polariser and the other as an analyser.

Turning to crystals, I found a large number of them exhibiting selective absorption in one direction. Of these nemalite and crysotile exhibit this property to a remarkable extent. Nermalite is a fibrous variety of brucite; crysotile being a variety of serpentine. The direction of absorption in these cases is parallel to the length, the direction of transmission being perpendicular to the length. I have here a piece of crysotile, only one inch in thickness. I adjust the polariser and the analyser parallel, and interpose the crysotile with its length parallel to the electric vibration. You observe that

the radiation is completely absorbed, none being transmitted. I now hold the piece with its length perpendicular to the electric vibration; the radiation is now copiously transmitted. Crysotile is thus seen to act as a perfect electric tourmaline.

*Anisotropic Conductivity exhibited by certain Polarising Substances.*

In a polarising grating, the electric vibrations perpendicular to the bars of the grating are alone transmitted, the vibrations parallel to the grating being absorbed or reflected. In a grating we have a structure which is not isotropic, for the electric conductivity parallel to the bars is very great, whereas the conductivity across the bars (owing to the interruptions due to spaces) is almost nothing. We may, therefore, expect electric vibrations parallel to the bars to produce local induction currents, which would ultimately be dissipated as heat. There would thus be no transmission of vibrations parallel to the grating, all such vibrations being absorbed. But owing to the break of metallic continuity, no induction current can take place across the grating; the vibrations in this direction are, therefore, transmitted. From these considerations we see how non-polarised vibrations falling on a grating would have the vibration components parallel to the direction of maximum conductivity absorbed, and those in the direction of least conductivity transmitted in a polarised condition.

I have shown that nemalite and crysotile polarise by selective absorption, the vibration perpendicular to their length being transmitted, and those parallel to their length being absorbed. Bearing in mind the relation between the double conductivity and double absorption, as exhibited by gratings, I was led to investigate whether the directions of the greatest and least absorptions in nemalite and crysotile were also the directions of maximum and minimum conductivities respectively. I found the conductivity of a specimen of nemalite in the direction of absorption to be about fourteen times the conductivity in the direction of transmission. In crysotile, too, the directions of the greatest and least absorption were also the directions of maximum and minimum conductivities.

It must, however, be noted that the substances mentioned above are bad conductors, and the difference of conductivity in the two directions is not anything like what we get in polarising gratings. A thin layer of nemalite or crysotile will, therefore, be unable to produce complete polarisation. But by the cumulative effect of many such layers in a thick piece, the vibrations which are perpendicular to the direction of maximum conductivity are alone transmitted, the emergent beam being thus completely polarised.

: A double-conducting structure will thus be seen to act as a polariser. I have here an artificial electric tourmaline, made of a bundle of parallel capillary glass fibres. The capillaries have been filled with dilute copper sulphate solution. A simple, and certainly the most handy,



polariser is one's outstretched fingers. I interpose my fingers at  $45^\circ$  between the crossed polariser and the analyser, and you observe the immediate restoration of the extinguished field of radiation. The double-conducting nature of the structure is here quite evident.

While repeating these experiments I happened to have by me this old copy of 'Bradshaw,' and it struck me that here was an excellent double-conducting structure which ought to polarise the electric ray. For looking at the edge of the book we see the paper continuous in one direction along the pages, whereas this continuity is broken across the pages by the interposed air-films. I shall now demonstrate the extraordinary efficiency of this book as an electric polariser. I hold it at  $45^\circ$  between the crossed gratings, and you observe the strong depolarisation effect produced. I now arrange the polariser and the analyser in a parallel position, and interpose the 'Bradshaw' with its edge parallel to the electric vibration; there is not the slightest action in the receiver, the book held in this particular direction being perfectly opaque to electric radiation. But on turning it round through  $90^\circ$ , the 'Bradshaw,' usually so opaque, becomes quite transparent, as is indicated by the violent deflection of the galvanometer-spot of light. An ordinary book is thus seen to act as a perfect polariser of the electric ray; the vibrations parallel to the pages are completely absorbed, and those at right angles transmitted in a perfectly polarised condition.

The electric radiation is thus seen to be reflected, refracted and polarised just in the same way as light is reflected, refracted and polarised. The two phenomena are identical. The anticipations of Maxwell have thus been verified by the great work of Hertz and his successors.

By pressing the key of this radiation apparatus I am able to produce ether vibrations, 30,000 millions in one second. A second stop in connection with another apparatus will give rise to a different vibration. Imagine a large electric organ provided with a very large number of stops, each key giving rise to a particular ether note. Imagine the lowest key producing one vibration in a second. We should then get a gigantic ether wave 186,000 miles long. Let the next key give rise to two vibrations in a second, and let each succeeding key produce higher and higher notes. Imagine an unseen hand pressing the different keys in rapid succession. The ether notes will thus rise in frequency from one vibration in a second, to tens, to hundreds, to thousands, to hundreds of thousands, to millions, to millions of millions. While the ethereal sea in which we are all immersed is being thus agitated by these multitudinous waves, we shall remain entirely unaffected, for we possess no organs of perception to respond to these waves. As the ether note rises still higher in pitch, we shall for a brief moment perceive a sensation of warmth. As the note still rises higher, our eye will begin to be affected, a red glimmer of light will be the first to make its appearance. From this point the few colours we see are comprised within a single octave

of vibration—from about 400 to 800 billions in one second. As the frequency of vibration rises still higher, our organs of perception fail us completely; a great gap in our consciousness obliterates the rest. The brief flash of light is succeeded by unbroken darkness.

These great regions of invisible lights are now being slowly and patiently explored. In time the great gaps which now exist will be filled up, and light-gleams, visible and invisible, will be found merging one into the other in unbroken sequence.

Before I conclude I may be permitted to express my sincere thanks to the managers of the Royal Institution for according me the privilege of addressing you this evening. I cannot sufficiently express my gratefulness for all the kindness I have received in this country. When the managers of this Institution, which has done so much to advance the cause of Science and Arts, invited me here, I felt that the scope of this great Institution was not merely confined to these shores, but embraced other countries, even the most distant. The land from which I come did at one time strive to extend human knowledge, but that was many centuries ago; a dark age has since supervened. It is now the privilege of the West to lead in this work. I would fain hope, and I am sure I am echoing your sentiments, that a time may come when the East, too, will take her part in this glorious undertaking; and that at no distant time it shall neither be the West nor the East, but both the East and the West, that will work together, each taking her share in extending the boundaries of knowledge, and bringing out the manifold blessings that follow in its train.

[J. C. B.]

Friday, March 12, 1897.

SIR FREDERICK ABEL, Bart. K.C.B. D.C.L. LL.D. F.R.S.  
Vice-President, in the Chair.

PROFESSOR ARTHUR SMITHELLS, B.Sc. F.I.C.

*The Source of Light in Flames.*

WHEN hydrogen burns in oxygen the gases unite to form steam, and a flame of simple structure is obtained. The light is of very feeble intensity, so feeble when the hydrogen is highly purified and when both gases are free from dust, that the flame is scarcely visible in a room from which all other light is excluded.\*

To what is the light of this flame due? It is not sufficient to say that it is the result of chemical action attended by the evolution of much heat. Light is of an undulatory nature, and the undulations arise during an oscillatory process associated with matter. We desire to know with what particular kind of atoms or molecules the light of a hydrogen flame is associated. It may be said that when hydrogen combines with oxygen the heat that is produced is necessarily contained, as it were, in the steam, and that therefore it is the steam that glows. This raises the question as to what evidence we have, apart from flames, of the possibility of making gases glow by the simple process of heating them. The evidence is nearly all negative. None of the common gases, including those contained in the best known flames, have been made to glow when heated by a purely baking or roasting process to the highest obtainable temperature. The passage of an electric discharge through the gases is not to be regarded as merely a heating process.

Among the gases that can be made to glow, the most conspicuous is iodine. The vapour of this substance shows a distinct red glow at a temperature below that at which glass is visibly red.† [Experiment shown.] It is possible that some chemical action, namely, dissociation and recombination, may be in progress in the iodine vapour, and that the emission of light may be due to this. A similar glow, however, has been obtained with bromine, and, to a less extent, with chlorine,‡ at temperatures which exclude the likelihood of dissociation.

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\* Stas, *Cœuvres*, tome iii. p. 228.

† Salet, '*Analyse Spectrale*,' p. 173; see also *Phil. Mag.* [v] 37, p. 245 (1894).

‡ Evershed, *Phil. Mag.* [v] 39, p. 460 (1895).

The great difficulty, and in most cases the present impossibility, of making gases glow by a mere increase of temperature of a direct kind, leads us to hesitate before we say that a hydrogen flame glows merely because it contains hot steam. The matter may be considered from another point of view. When hydrogen burns, the atoms of hydrogen are combining chemically with atoms of oxygen. It is impossible to picture this process with any certainty of detail, but we do know that the uncombined atoms have a store of energy which is set free or becomes perceptibly kinetic when they combine. This action takes place only when the atoms are within each other's sphere of chemical attraction, or, in other words, when the new substance begins to be formed. It seems impossible not to suppose that such a process entails in the substance that is being formed a condition as regards motion which must be considered apart from any condition of temperature which is exhibited by the flame as a whole. We cannot suppose, when a number of atoms commence to form a molecular system, that the liberation of their potential energy will result directly in increased translatory motion of the newly formed molecule. The process may be compared to two oppositely electrified spheres approaching one another rapidly in space in paths sufficiently close for the mutual attraction to determine their union into a system of revolution ending in actual contact. During the coalescence the system would be in a vibratory state.

Without propounding any hypothesis as to the nature of chemical energy, it seems certain that in the process of chemical union the newly formed substance is in a state that it will be very difficult, and perhaps even impossible, for it to acquire by what we ordinarily understand as an increase of temperature, and this state being oscillatory may well occasion the emission of light.

The oscillatory motion will be short lived and will disappear in two ways, first in producing radiations, and secondly and chiefly, in communicating to other impinging molecules, and thereby to itself, an increased translatory motion which corresponds to increase of temperature. According to this view the emission of light by a burning gas is antecedent to, rather than consequent upon, a high temperature, if we used this last term in its ordinary sense.

If the number of molecules being formed in a flame at any instant is small compared with the number of other molecules in their immediate neighbourhood, we may have a flame in which the emission of light is associated with a low general temperature. This case arises with substances that enter into combination freely at low temperatures. A stream of carbon dioxide charged with a little phosphorus vapour produces a bright green flame when it issues into the air. The light is due to phosphoric oxide, that is to say, it is the formation of phosphoric oxide that occasions it. Much energy is liberated during the formation of each molecule, but the luminous molecules are so far apart, there are so many molecules of carbon dioxide round them, that the average temperature is quite incon-

siderable, and the finger perceives no heat when held in the flame. If the supply of phosphorus vapour be increased the number of luminous molecules increases, the light becomes brighter, and the temperature also rises in due proportion.

In the case of hydrogen, which does not ignite at a low temperature, it is impossible to get a cool sheet of flame, for by the addition of a neutral gas, the molecules of nascent steam are soon separated to such an extent that the energy liberated is insufficient to keep the general temperature of the sheet up to the point required to stimulate sufficiently the combination of the incoming hydrogen.

If the shell of burning gas, which constitutes what may be called the foundation of a flame, is very hot, it is always possible that a secondary source of light may be developed, due to a purely baking process. This may affect the product of combustion itself, or the unburned gas or some decomposition product. We might thus anticipate that in the hydrogen flame light would come not only from the steam, which is being formed, but also from the hydrogen within the flame, which is subjected to intense roasting as it ascends. This, however, does not appear to be the case. The occurrence of the spectrum of hydrogen in that of the oxy-hydrogen flame was described by Plücker, but experiments undertaken by Professor Liveing,\* specially to test this question, have decided it in the negative. The light of the oxy-hydrogen flame has been examined spectroscopically by Professors Liveing and Dewar, Dr. Huggins and others, and the spectrum is now attributed to water alone:

The light of a hydrogen flame is very feeble compared with that of most other flames. If we ask why this is so, we are asking almost the same question that eighty years ago impelled Sir Humphry Davy to the splendid researches which laid the foundation of our scientific knowledge of flames. And it was the same question that fifty years later led Dr. Edward Frankland to investigations of flame, which rank second only to those of his illustrious predecessor. Curious to know why an explosive mixture of coal gas and air within a safety lamp burned with a pale blue flame, whilst coal gas ordinarily burnt with a bright light, Davy, after a few simple experiments, concluded that he was correct in his first surmise, viz. "that the cause of the superiority of the light from the *stream* of coal-gas might be owing to a *decomposition* of a part of the gas towards the interior of the flame where the air was in smallest quantity, and the deposition of solid charcoal which, first by its *ignition* and afterwards by its *combustion*, increased in a high degree the intensity of the light." Davy's final and general conclusion was that "whenever a flame is remarkably brilliant or dense it may be always concluded that some solid matter is produced in it; on the contrary, when a flame is extremely feeble and transparent it may be inferred that no solid matter is formed."

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\* Phil. Mag. [v] 34, p. 371 (1892).

In 1867 Dr. Frankland, lecturing before the Royal Institution,\* gave strong reasons for dissenting from Davy's views, both as to the cause of the luminosity of flames in general and of the flames of hydrocarbons in particular. Dr. Frankland's conclusions may be summarised as follows :—

- (i.) Bright flames exist which do not contain solid particles.
- (ii.) The luminosity of flames depends mainly on the density of the substances contained in them.
- (iii.) Feebly luminous flames may be made bright by compressing the burning gases.
- (iv.) The luminosity of ordinary hydrocarbon flames, such as that of coal gas, is not due in any important degree to solid particles of carbon, but almost entirely to the glow of dense hydrocarbon vapours.

Of these conclusions, two are beyond doubt. The flame of phosphorus, or of carbon-disulphide burning in oxygen, are examples of bright flames in which no solid matter can be supposed reasonably to exist. The explosion of electrolytic gas in a eudiometer resting on an india-rubber pad produces a bright light, the gas is hindered from expanding, and hence the flame travels through the mixture under increasing pressure.

A table, in Dr. Frankland's paper, shows the kind of evidence from which he concluded that the brightness of flames depends on the density of the substances they contain, and the general agreement of fact with theory is very striking. It is important to know whether the rule holds without exception, and whether it is in harmony with other general laws. There are flames containing dense substances which are not bright, and flames which are bright though they do not contain dense substances; but these apparent exceptions are explained by supposing that the temperature in one case is very low and in the other very high. If this kind of accommodation is permissible, Dr. Frankland's principle can hardly be submitted to a rigorous test.

The fact that the light of compressed flames is so intense can hardly be held to support the general doctrine in any rational sense, for it cannot be said either physically or chemically that two gases are in a like state when they have the same density. As a *fact* the increased luminosity here accompanying increased density is undeniable, and Dr. Frankland has contended for no more than this; but the matter must be looked at in the light of the molecular theory. This theory would lead us to expect increased light from a flame containing dense matter if the density were a result of molecular crowding, whilst it can at present tell us nothing about the effect likely to ensue from an increase of density arising from the greater

\* Proc. Roy. Inst. 5, p. 419. The best account of Dr. Frankland's views is contained in six lectures delivered at the Royal Institution, and admirably reported in the 'Journal of Gas Lighting.'

weight of the individual molecules. For this reason Dr. Frankland's observations on compressed flames may be considered essentially unconnected with the observations on uncompressed flames containing substances of high molecular weight, though the results may be embodied in a single statement; and to this extent the generalisation loses importance.

The development of brightness in a flame may be conveniently studied in the flame of hydrogen phosphide. When this gas is sufficiently diluted with carbon dioxide, the flame has the same green glow as has been already noticed in the case of carbon dioxide charged with phosphorus vapour. This glow is to be ascribed to the formation of an oxide of phosphorus, and since phosphorus oxide itself glows in presence of oxygen with exactly the same light,\* we may reasonably conclude that the oxide whose formation determines the glow is the pentoxide. If now the proportion of hydrogen phosphide to carbon dioxide be slightly increased, an entirely new kind of luminosity is developed in the flame towards the tip. This is at first yellowish, but increases in whiteness and brilliance as the supply of carbon dioxide is diminished, until finally, when the pure hydride is burning, the flame has the appearance of brightly burning phosphorus. This yellow or white light is to be regarded as secondary in origin, and to be the result of high temperature in the ordinary sense of the word. In confirmation of this it may be stated that the light appears in exactly that place where, considering the flame as a heating agent, the effective temperature would be highest; and further, if a ring of copper wire be placed horizontally in the lower part of the flame, so as to lower the general temperature, the yellow luminosity at once disappears just as it does when the flame is cooled by an increase in the supply of carbon dioxide. It is a matter of much interest to determine what substance emits the yellow or white light. It might be supposed to be due to phosphorus separated within the flame by decomposition of the hydrogen phosphide. In that case the introduction of oxygen into the middle of the flame might be expected to diminish the luminosity; but the reverse is the case. The glow appears to be due to phosphorus pentoxide, for if the flame of a Bunsen burner be held above the hydrogen phosphide flame the yellow-white glow is extended continuously upwards into the Bunsen flame. The track of the phosphorus pentoxide can in fact be seen in the form of a white glow so long as the temperature of the surroundings reaches a certain point. The absence of solid particles from a hydrogen phosphide flame can be shown by concentrating the sun's rays upon it.

In these experiments the use of hydrogen phosphide gives a convenient method of regulating the supply of phosphorus; they may be repeated with phosphorus vapour itself diluted with carbon dioxide, and the same results are obtained. It appears, therefore, that there

are two luminous effects to recognise in the combustion of phosphorus. One is due to the act of formation of phosphorus pentoxide giving the green glow, and the other due to the subsequent heating of the same substance producing the white glow. Adopting the terminology suggested by E. Wiedemann, we may say that there is chemi-luminescence and thermo-luminescence of phosphorus pentoxide. In what is ordinarily called the phosphorescence of phosphorus we have the chemi-luminescence; in the vivid combustion of phosphorus the chemi-luminescence is completely overpowered and masked by the thermo-luminescence.

It is interesting to inquire how far other combustible elements behave in the same way. The flame of silicon hydride may be subjected to similar experiments. When sufficiently diluted with carbon dioxide a pale greenish flame is obtained, silica being the product. The green colour may therefore be attributed to the formation of this compound. When the supply of carbon dioxide is reduced the flame becomes brightly luminous, but the luminosity may be removed by cooling with a wire ring. The optical test shows the bright light to be due to solid particles, and as the glow is prolonged continuously in the track of the escaping silica when a Bunsen flame is held over the silicon hydride flame, it seems clear that the secondary or bright luminosity of the flame is here, as in the case of phosphorus, to be ascribed to a purely thermal action. The chief difference in the two instances is that in the case of phosphorus hydride the product is a glowing gas, and in the case of silicon hydride a glowing solid.

Hydrocarbon flames may also be considered from the same point of view, and here the facts are well known. In the first instance we have to recognise in a hydrocarbon flame the bright yellow light and the blue or lilac light. The bright yellow light may be suppressed by cooling by means of a wire or by diluting the gas with carbon dioxide. This part of the light of a hydrocarbon flame has frequently been ascribed to a preferential burning of the hydrogen, whereby carbon is separated in the flame and glows in the state of solid particles. This view, which appears to have originated in a misinterpretation of Davy's words, has never been based on substantial evidence, and it is at variance with the most cogent experiments on the subject. There seems little doubt that the bright glow of a hydrocarbon flame is essentially a thermal phenomenon.

The glowing substance was supposed by Davy to be solid particles of carbon, by Frankland to be the vapour of dense hydrocarbons. These two rival views have been subject to considerable discussion, especially by Heumann.\*

It seems extremely difficult now to find any good evidence for the dense hydrocarbon theory. One of the simplest arguments against it was supplied by Stein, who pointed out that the glowing



substance in a hydrocarbon flame, which may be collected in the form of soot, contains a smaller quantity of hydrogen than could reasonably be expected if soot were a hydrocarbon or a mixture of hydrocarbons. He also remarked upon the non-volatile character of soot. A recent analysis of soot from an acetylene flame showed 1.4 parts of hydrogen to 98.6 parts of carbon, after the soot had been extracted with ether and dried. Now the hydrocarbon richest in carbon recognised in organic chemistry (chrysogene) contains about 5 per cent. of hydrogen. The soot, therefore, could not contain more than about 30 per cent. of it, leaving a surplus of 70 per cent. of uncombined carbon. To maintain Frankland's doctrine that the light is essentially due to dense hydrocarbons in the gaseous state, would compel us, in fact, to recognise soot as a hydrocarbon of quite exceptional composition and properties. The doctrine was, in its inception, an inference from experiments on other flames in which high luminosity was found to be associated with high density of the substances contained in the flames; but it is to be remarked that in most, if not all of these flames, the glow was ascribed to the product of oxidation, and not merely to something separated and subjected to a purely roasting process.

But even if we regard the glowing substance soot of a flame as a hydrocarbon or a mixture of hydrocarbons, and to this extent accept Frankland's view, there remains the question whether the glowing substance in the flame is solid or gaseous. The optical test, first used by Soret, shows indisputably that a finely divided solid pervades the whole of the luminous region of a hydrocarbon flame, and there seems no reason to doubt that the glow of this solid matter would be adequate to produce the light of the flame.

According to the views of Lewes, the luminosity of a hydrocarbon flame is determined essentially by the formation and subsequent decomposition of acetylene. This theory, which is certainly ingenious, need not be discussed on the present occasion.

The development of bright light in a hydrocarbon flame, whatever be the full explanation, is certainly a secondary process, demanding a particular mode of burning the gas for its production. When the hydrocarbon meets the air in other ways, as when it is burnt in a very small flame or at a very high pressure, or when air is added to the gas before it leaves the burner, the bright light disappears, and we then have the primary light of combustion which is of feeble intensity and blue colour. The changes which a hydrocarbon flame undergoes with varying air supply are well seen when benzene vapour is burned with a gradually increasing quantity of admixed air. The flame is at first very bright; the next phase, reached when the bright yellowish light has just disappeared, shows two cones of bluish light, corresponding to those of a Bunsen burner; the last phase is reached when, by adding more air, the outer cone is quenched, and the flame presents the appearance of a thin conical shell of blue light. [Experiment shown.] The two-coned phase

marks the period when the oxygen required for combustion is got partly from the air mixed with the vapour before it leaves the burner and partly from the air outside, one cone corresponding to each part of the supply. From analyses of the interconal gases, it appears that large quantities of carbon monoxide and hydrogen are generated in the inner cone, and that these are the gases which burn in the outer cone. The evidence that the formation of carbon monoxide is the first step in the combustion of carbon has been greatly strengthened by the experiments of Prof. H. B. Dixon, and is at variance with no important facts.

The source of the light in a blue-burning hydrocarbon flame has been the subject of most elaborate investigation and of prolonged controversy. The spectrum of this light was one of the first to be carefully described, and is often called the Swan spectrum, from the fact that it was first accurately mapped by Swan in 1856. It is seen in the blue part at the base of all ordinary hydrocarbon flames and in the inner cone, but not in the outer cone of flames fed with air in the manner of the Bunsen burner. In so far as the characteristic product of these parts of flames has been found to be carbonic oxide, it would be natural to attribute the Swan spectrum to this gas. This view, however, has never been adopted. The Swan spectrum has been attributed either to carbon itself or to a hydrocarbon (acetylene), and the whole discussion and investigation of the subject has centred round these alternatives. The neglect to consider the likelihood of carbon monoxide being the source has arisen from a disregard of the occurrence of this gas in flames, and from a belief that it has another distinct spectrum. At the same time the difficulty presented by the other explanations has been fully realised, and it is admitted that the support of either demands somewhat strained hypotheses.

The question of the origin of the Swan spectrum is too large and complicated to be fully discussed here. It will suffice to point out that if the formation of carbon monoxide is the first act in the oxidation of a hydrocarbon two results would follow: (1) it would hardly be supposed that carbon vapour existed free even momentarily in the flame; (2) that the preponderating product with which was associated the energy of the chemical change should contribute mainly to the emission of light. The chief difficulty opposed to the view that carbon monoxide is really the source of the Swan spectrum appears to lie in the fact that this gas may be made to yield a different spectrum by the electric discharge. A full consideration of the evidence bearing on the subject leads to the view, first, that this spectrum is not undoubtedly due to carbon monoxide, and secondly, that it may be due to carbon dioxide.

The evidence derived from the study of flames, and much other evidence, is favourable to the view that carbon monoxide is the source of the Swan spectrum, and if this be the case, the chemi-luminescence of a hydrocarbon flame like that of a flame of the hydrides of phosphorus, silica and antimony, would be attributed to the act of oxidation.

Some light is no doubt due to the completion of the oxidation, the carbon monoxide forming carbon dioxide and the hydrogen forming water, but the intensity of this portion of the light is inconsiderable in the spectroscope, and in the visible spectrum not characteristic.

The flame of cyanogen presents special points of interest. It has been shown that the sharp differentiation of the flame into an inner rose-coloured cone and an outer blue one, corresponds to the combustion of the gas in two steps, the first being the oxidation of carbon to carbon monoxide, and the second the oxidation of carbon monoxide to carbon dioxide.\* Admixture of air with the gas before combustion renders it possible to separate the two parts of the flame in the cone separating apparatus, and when the distance between them exceeds a certain limit and the gases are dried, the outer cone is quenched when a bottle of dried air is held over it. [Experiment shown.] This behaviour accords with the well known experiment of Prof. Dixon on the combustion of carbon monoxide. According to the view which has been developed in the foregoing, it would be expected that the light emitted by the inner cone of a cyanogen flame should be due to the carbon monoxide which is produced there, and if the Swan spectrum be really due to that substance then the Swan spectrum should be seen. As a matter of fact, the inner cone of a cyanogen flame gives a brilliant spectrum, in which, however, only one band of the Swan spectrum is distinctly developed. It is possible that the liberation of nitrogen from cyanogen during its combustion may have a disturbing influence. In any case it is very striking that when cyanogen is burnt in oxygen instead of air the Swan spectrum is seen to be completely and brilliantly developed, and on the whole the evidence derived from a cyanogen flame appears to strengthen the view which associates the Swan spectrum with the production of carbon monoxide.

Reviewing the evidence which has been offered, it appears that the primary source of light in flames is to be found in the intense vibratory motion which is determined by the act of chemical union. This is seen in the phosphorescence of phosphorus, in the flame of hydrogen, and at the base of the flames of the hydrides of silicon and carbon. A secondary source of light arises when the temperature effect of the primary combustion causes the glow of a product or partial product of combustion. This is seen in the white flame of phosphorus, in the brightest part of the flame of silicon hydride, and in the bright yellow-white part of ordinary hydrocarbon flames.

The question of the luminosity of flames containing the vapours of salts introduces new problems, the elucidation of which is far from being complete. This question, however, cannot be considered on the present occasion.

[A. S.]

\* Smithells and Dent, Journ. Chem. Soc. 65, p. 603 (1894).

Friday, April 30, 1897.

SIR FRÉDÉRIK BRAMWELL, Bart. D.C.L. LL.D. F.R.S. Honorary  
Secretary and Vice-President, in the Chair.

PROFESSOR J. J. THOMSON, M.A. LL.D. Sc.D. F.R.S.

*Cathode Rays.*

THE first observer to leave any record of what are now known as the Cathode Rays seems to have been Plücker, who in 1859 observed the now well known green phosphorescence on the glass in the neighbourhood of the negative electrode. Plücker was the first physicist to make experiments on the discharge through a tube, in a state anything approaching what we should now call a high vacuum: he owed the opportunity to do this to his fellow townsman Geissler, who first made such vacua attainable. Plücker, who had made a very minute study of the effect of a magnetic field on the ordinary discharge which stretches from one terminal to the other, distinguished the discharge which produced the green phosphorescence from the ordinary discharge, by the difference in its behaviour when in a magnetic field. Plücker ascribed these phosphorescent patches to currents of electricity which went from the cathode to the walls of the tube, and then for some reason or other retraced their steps.

The subject was next taken up by Plücker's pupil, Hittorf, who greatly extended our knowledge of the subject, and to whom we owe the observation that a solid body placed between a pointed cathode and the walls of the tube cast a well defined shadow. This observation was extended by Goldstein, who found that a well marked, though not very sharply defined shadow was cast by a small body placed near a cathode of considerable area; this was a very important observation, for it showed that the rays casting the shadow came in a definite direction from the cathode. If the cathode were replaced by a luminous disc of the same size, this disc would not cast a shadow of a small object placed near it, for though the object might intercept the rays which came out normally from the disc, yet enough light would be given out sideways from other parts of the disc to prevent the shadow being at all well marked. Goldstein seems to have been the first to advance the theory, which has attained a good deal of prevalence in Germany, that these cathode rays are transversal vibrations in the ether.

The physicist, however, who did more than any one else to direct attention to these rays was Mr. Crookes, whose experiments, by their beauty and importance, attracted the attention of all physicists to this

subject, and who not only greatly increased our knowledge of the properties of the rays, but by his application of them to radiant matter spectroscopy has rendered them most important agents in chemical research.

Recently a great renewal of interest in these rays has taken place, owing to the remarkable properties possessed by an offspring of theirs, for the cathode rays are the parents of the Röntgen rays.

I shall confine myself this evening to endeavouring to give an account of some of the more recent investigations which have been made on the cathode rays. In the first place, when these rays fall on a substance they produce changes physical or chemical in the nature of the substance. In some cases this change is marked by a change in the colour of the substance, as in the case of the chlorides of the alkaline metals. Goldstein found that these when exposed to the cathode rays changed colour, the change, according to E. Wiedemann and Ebert, being due to the formation of a subchloride. Elster and Geitel have recently shown that these substances become photo-electric, i.e. acquire the power of discharging negative electricity under the action of light, after exposure to the cathode rays. But though it is only in comparatively few cases that the change produced by the cathode rays shows itself in such a conspicuous way as by a change of colour, there is a much more widely spread phenomenon which shows the permanence of the effect produced by the impact of these rays. This is the phenomenon called by its discoverer, Prof. E. Wiedemann, thermoluminescence. Prof. Wiedemann finds that if bodies are exposed to the cathode rays for some time, when the bombardment stops the substance resumes to all appearance its original condition; when, however, we heat the substance, we find that a change has taken place, for the substance now, when heated, becomes luminous at a comparatively low temperature, one far below that of incandescence; the substance retains this property for months after the exposure to the rays has ceased. The phenomenon of thermoluminescence is especially marked in bodies which are called by Van t'Hoff solid solutions; these are formed when two salts, one greatly in excess of the other, are simultaneously precipitated from a solution. Under these circumstances the connection between the salts seems of a more intimate character than that existing in a mechanical mixture. I have here a solid solution of  $\text{CaSO}_4$  with trace of  $\text{MnSO}_4$ , and you will see that after exposure to the cathode rays it becomes luminous when heated. Another proof of the alteration produced by these rays is the fact, discovered by Crookes, that after glass has been exposed for a long time to the impact of these rays, the intensity of its phosphorescence is less than when the rays first began to fall upon it. This alteration lasts for a long time, certainly for months, and Mr. Crookes has shown that it is able to survive the heating up of the glass to allow of the remaking of the bulb. I will now leave the chemical effects produced by these rays, and pass on to consider their behaviour when in a magnetic field.

First, let us consider for a moment the effect of magnetic force on the ordinary discharge between terminals at a pressure much higher than that at which the cathode rays begin to come off. I have

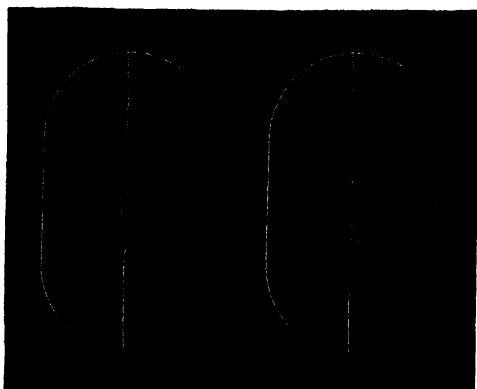


FIG. 1.

FIG. 2.

here photographs (see Figs. 1 and 2) of the spark in a magnetic field. You see that when the discharge, which passes as a thin bright line between the terminals, is acted upon by the magnetic field; it is pulled aside as a stretched string would be if acted upon by a force at right

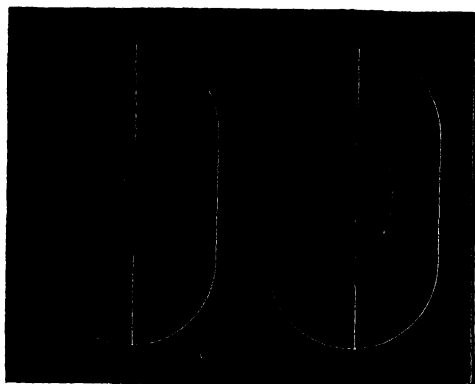


FIG. 3.

FIG. 4.

angles to its length. The curve is quite continuous, and though there may be gaps in the luminosity of the discharge, yet there are no breaks at such points in the curve, into which the discharge is bent by

a magnet. Again, if the discharge, instead of taking place between points, passes between flat discs, the effect of the magnetic force is to move the sparks as a whole, the sparks keeping straight until their terminations reach the edges of the discs. The fine thread-like discharge is not much spread out by the action of the magnetic field. The appearance of the discharge indicates that when the discharge passes through the gas it manufactures out of the gas something stretching from terminal to terminal, which, unlike a gas, is capable of sustaining a tension. The amount of deflection produced, other circumstances being the same, depends on the nature of the gas; as the photographs (Figs. 3 and 4) show, the deflection is very small in the case of hydrogen, and very considerable in the case of carbonic acid; as a general rule it seems smaller in elementary than in compound gases.

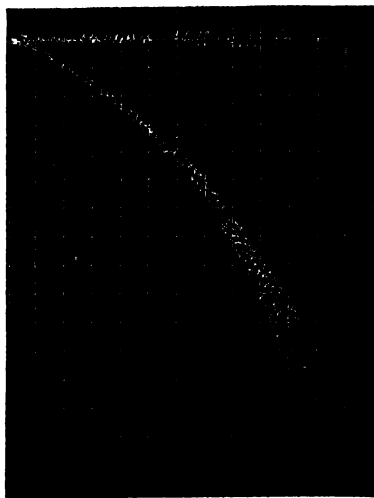


FIG 5.—Hydrogen (Ammeter, 12 ; Voltmeter, 1600).

Let us contrast the behaviour of this kind of discharge under the action of a magnetic field with that of the cathode rays. I have here some photographs (Figs 5, 6 and 7) taken of a narrow beam formed by sending the cathode rays through a tube in which there was a plug with a slit in it, the plug being used as an anode and connected with the earth, these rays traversing a uniform magnetic field. The narrow beam spreads out under the action of the magnetic force into a broad fan-shaped luminosity in the gas. The luminosity in this fan is not uniformly distributed, but is condensed along certain lines. The phosphorescence produced when the rays reach the glass is also not uniformly distributed; it is much spread out, showing that the beam consists of rays which are not all deflected to the same extent

by the magnet. The luminous patch on the glass is crossed by bands along which the luminosity is very much greater than in the adjacent

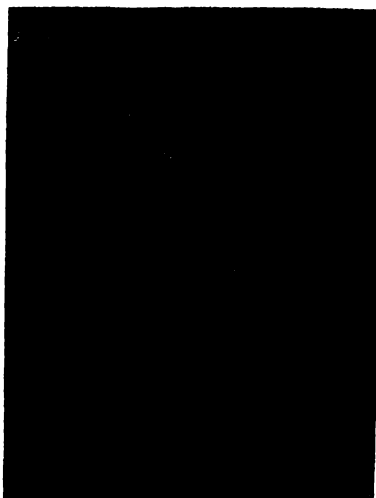


FIG. 6.—Air.



FIG. 7.—Carbonic Acid Gas (Ammeter, 12; Voltmeter, 1600)<sup>1</sup>/<sub>4</sub>

parts. These bright and dark bands are called by Birkeland, who first observed them, "the magnetic spectrum." The brightest places



on the glass are by no means always the terminations of the brightest streaks of luminosity in the gas; in fact, in some cases a very bright spot on the glass is not connected with the cathode by any appreciable luminosity, though there is plenty of luminosity in other parts of the gas.

One very interesting point brought out by the photographs is that in a given magnetic field, with a given mean potential difference between the terminals, the path of the rays is independent of the nature of the gas; photographs were taken of the discharge in hydrogen, air, carbonic acid, methyl iodide, i.e. in gases whose densities range from 1 to 70, and yet not only were the paths of the most deflected rays the same in all cases, but even the details, such as the distribution of the bright and dark spaces, were the same; in fact, the photographs could hardly be distinguished from each other. It is to be noted that the pressures were not the same; the pressures were adjusted until the mean potential difference was the same. When the pressure of the gas is lowered, the potential difference between the terminals increases, and the deflection of the rays produced by a magnet diminishes, or at any rate the deflection of the rays where the phosphorescence is a maximum diminishes. If an air break is inserted in the circuit an effect of the same kind is produced. In all the photographs of the cathode rays one sees indications of rays which stretch far into the bulb, but which are not deflected at all by a magnet. Though they stretch for some two or three inches, yet in none of these photographs do they actually reach the glass. In some experiments, however, I placed inside the tube a screen, near to the slit through which the cathode rays came, and found that no appreciable phosphorescence was produced when the non-deflected rays struck the screen, while there was vivid phosphorescence at the places where the deflected rays struck the screen. These non-deflected rays do not seem to exhibit any of the characteristics of cathode rays, and it seems possible that they are merely jets of uncharged luminous gas shot out through the slit from the neighbourhood of the cathode by a kind of explosion when the discharge passes.

The curves described by the cathode rays in a uniform magnetic field are, very approximately at any rate, circular for a large part of their course; this is the path which would be described if the cathode rays marked the path of negatively electrified particles projected with great velocities from the neighbourhood of the negative electrode. Indeed, all the effects produced by a magnet on these rays, and some of these are complicated, as, for example, when the rays are curled up into spirals under the action of a magnetic force, are in exact agreement with the consequences of this view.

We can, moreover, show by direct experiment that a charge of negative electricity follows the course of the cathode rays. One way in which this has been done is by an experiment due to Perrin, the details of which are shown in the accompanying figure (Fig. 8.) In this experiment the rays are allowed to pass inside a metallic cylinder

through a small hole, and the cylinder, when these rays enter it, gets a negative charge, while if the rays are deflected by a magnet, so as to escape the hole, the cylinder remains without charge. It seems to me that to the experiment in this form it might be objected that, though the experiment shows that negatively electrified bodies are projected normally from the cathode, and are deflected by a magnet, it does not show that when the cathode rays are deflected by a magnet the path of the electrified particles coincides with the path of the cathode rays. The supporters of the theory that these rays are waves

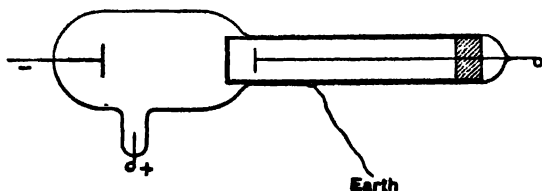


FIG. 8.

in the ether might say, and indeed have said, that while they did not deny that electrified particles might be shot off from the cathode, these particles were, in their opinion, merely accidental accompaniments of the rays, and were no more to do with the rays than the bullet has with the flash of a rifle. The following modification of Perrin's experiment is not, however, open to this objection: Two co-axial cylinders (Fig. 9), with slits cut in them, the outer cylinder being connected with earth, the inner with the electrometer, are placed in the discharge tube, but in such a position that the cathode

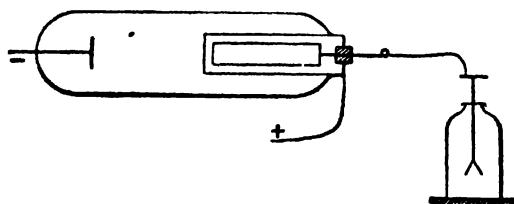


FIG. 9.

rays do not fall upon them unless deflected by a magnet; by means of a magnet, however, we can deflect the cathode rays until they fall on the slit in the cylinder. If under these circumstances the cylinder gets a negative charge when the cathode rays fall on the slit, and remains uncharged unless they do so, we may conclude, I think, the stream of negatively-electrified particles is an invariable accompaniment of the cathode rays. I will now try the experiment. You notice that when there is no magnetic force, though the rays do not fall on the cylinder, there is a slight deflection of the electrometer,

showing that it has acquired a small negative charge. This is, I think, due to the plug getting negatively charged under the torrent of negatively electrified particles from the cathode, and getting out cathode rays on its own account which have not come through the slit. I will now deflect the rays by a magnet, and you will see that at first there is little or no change in the deflection of the electrometer, but that when the rays reach the cylinder there is at once a great increase in the deflection, showing that the rays are pouring a charge of negative electricity into the cylinder. The deflection of the electrometer reaches a certain value and then stops and remains constant, though the rays continue to pour into the cylinder. This is due to the fact that the gas traversed by the cathode rays becomes a conductor of electricity, and thus, though the inner cylinder is perfectly insulated when the rays are not passing, yet as soon as the rays pass through the bulb the air between the inner cylinder and the outer one, which is connected with the earth, becomes a conductor, and the electricity escapes from the inner cylinder to the earth. For this reason the charge within the inner cylinder does not go on continually increasing: the cylinder settles into a state of equilibrium in which the rate at which it gains negative electricity from the rays is equal to the rate at which it loses it by conduction through the air. If we charge up the cylinder positively it rapidly loses its positive charge and acquires a negative one, while if we charge it up negatively it will leak if its initial negative potential is greater than its equilibrium value.

I have lately made some experiments which are interesting from the bearing they have on the charges carried by the cathode rays, as well as on the production of cathode rays outside the tube. The experiments are of the following kind. In the tube (Fig. 10) A and B are terminals. C is a long side tube into which a closed metallic cylinder fits lightly. This cylinder is made entirely of metal except the end furthest from the terminals, which is stopped by an ebonite plug, perforated by a small hole so as to make the pressure inside the cylinder equal to that in the discharge tube. Inside the cylinder there is a metal disc supported by a metal rod which passes through the ebonite plug, and is connected with an electrometer, the wires making this connection being surrounded by tubes connected with the earth so as to screen off electrostatic induction. If the end of the cylinder is made of thin aluminium about  $\frac{1}{10}$ th of a millimetre thick, and a discharge sent between the terminals, A being the cathode, then at pressures far higher than those at which the cathode rays come off, the disc inside the cylinder acquires a positive charge. And if it is charged up independently the charge leaks away, and it leaks more rapidly when the disc is charged negatively than when it is charged positively; there is, however, a leak in both cases, showing that conduction has taken place through the gas between the cylinder and the disc. As the pressure in the tube is diminished the positive charge on the disc diminishes until it becomes unappreciable. The

leak from the disc when it is charged still continues, and is now equally rapid, whether the original charge on the disc is positive or negative. When the pressure falls so low that cathode rays begin to fall on the end of the cylinder, then the disc acquires a negative charge, and the leak from the disc is more rapid when it is charged positively than when it is charged negatively. If the cathode rays are pulled off the end of the cylinder by a magnet, then the negative charge on the disc and the rate of leak from the disc when it is positively charged is very much diminished. A very interesting point is that these effects, due to the cathode rays, are observed behind comparatively thick walls. I have here a cylinder whose base is brass about 1 mm. thick, and yet when this is exposed to the cathode rays the disc behind it gets a negative charge, and leaks if charged positively. The effect is small compared with that in the cylinder with the thin aluminium base, but is quite appreciable. With the cylinder with the thick end I have never been able to observe any effect at the higher pressures when no cathode rays were coming off. The effect with the cylinder with the thin end was observed when the discharge was produced by a large number of small storage cells, as well as when it was produced by an induction coil.

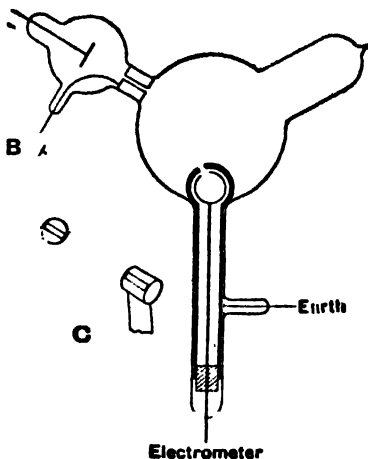


FIG. 10.

It would seem from this experiment that the incidence of the cathode rays on a brass plate as much as 1 mm. thick, and connected with the earth, can put a rarefied gas shielded by the plate into a condition in which it can conduct electricity, and that a body placed behind this screen gets a negative charge, so that the side of the brass away from the cathode rays acts itself like a cathode though kept permanently to earth. In the case of the thick brass the effect seems much more likely to be due to a sudden change in the potential of the outer cylinder at the places where the rays strike, rather than to the penetration of any kinds of waves or rays. If the discharge in the tube was perfectly continuous the potential of the outer cylinder would be constant, and since it is connected to earth by a wire through which no considerable current flows, the potential must be approximately that of the earth. The discharge there cannot be continuous; the negative charge must come in gusts against the ends of the cylinder, coming so suddenly that the electricity has no time to distribute itself over the cylinder so as to shield off the inside from the

electrostatic action of the cathode rays; this force penetrates the cylinder and produces a discharge of electricity from the far side of the brass.

Another effect which I believe is due to the negative electrification carried by the rays is the following. In a very highly exhausted tube provided with a metal plug, I have sometimes observed, after the coil has been turned off, bright patches on the glass; these are deflected by a magnet, and seem to be caused by the plug getting such a large negative charge that the negative electricity continues to stream from it after the coil is stopped.

An objection sometimes urged against the view that these cathode rays consist of charged particles, is that they are not deflected by an electrostatic force. If, for example, we make, as Hertz did, the rays pass between plates connected with a battery, so that an electrostatic force acts between these plates, the cathode ray is able to traverse this space without being deflected one way or the other. We must remember, however, that the cathode rays, when they pass through a gas make it a conductor, so that the gas acting like a conductor screens off the electric force from the charged particle, and when the plates are immersed in the gas, and a definite potential difference established between the plates, the conductivity of the gas close to the cathode rays is probably enormously greater than the average conductivity of the gas between the plates, and the potential gradient on the cathode rays is therefore very small compared with the average potential gradient. We can, however, produce electrostatic results if we put the conductors which are to deflect the rays in the dark space next the cathode. I have here a tube in which, inside the dark space next the cathode, two conductors are inserted; the cathode rays start from the cathode and have to pass between these conductors; if, now, I connect one of these conductors to earth there is a decided deflection of the cathode rays, while if I connect the other electrode to earth there is a deflection in the opposite direction. I ascribe this deflection to the gas in the dark space either not being a conductor at all, or if a conductor, a poor one compared to the gas in the main body of the tube.

Goldstein has shown that if a tube is furnished with two cathodes, when the rays from one cathode pass near the other they are repelled from it. This is just what would happen if the dark space round the electrode were an insulator, and so able to transmit electrostatic attractions or repulsions. To show that the gas in the dark space differs in its properties from the rest of the gas, I will try the following experiment. I have here two spherical bulbs connected together by a glass tube; one of these bulbs is small, the other large; they each contain a cathode, and the pressure of the gas is such that the dark space round the cathode in the small bulb completely fills the bulb, while that round the one in the larger bulb does not extend to the walls of the bulb. The two bulbs are wound with wire, which connects the outsides of two Leyden jars; the insides of these jars

are connected with the terminals of a Wimshurst machine. When sparks pass between these terminals currents pass through the wire which induce currents in the bulbs, and cause a ring discharge to pass through them. Things are so arranged that the ring is faint in the larger bulb, bright in the smaller one. On making the wires in these bulbs cathodes, however, the discharge in the small bulb, which is filled by the dark space, is completely stopped, while that in the larger one becomes brighter. Thus the gas in the dark space is changed, and in the opposite way from that in the rest of the tube. It is remarkable that when the coil is stopped the ring discharge on both bulbs stops, and it is some time before it starts again.

The deflection excited on each other by two cathodic streams would seem to have a great deal to do with the beautiful phosphorescent figures which Goldstein obtained by using cathodes of different shapes. I have here two bulbs containing cathodes shaped like a cross; they are curved, and of the same radius as the bulb, so that if the rays came off these cathodes normally the phosphorescent picture ought to be a cross of the same size as the cathode, instead of being of the same size. You see that in one of these bulbs the image of the cross consists of two large sectors at right angles to each other, bounded by bright lines, and in the other, which is at a lower pressure, the geometrical image of the cross, instead of being bright, is dark, while the luminosity occupies the space between the arms of the cross.

So far I have only considered the behaviour of the cathode rays inside the bulb, but Lenard has been able to get these rays outside the tube. To this he let the rays fall on a window in the tube, made of thin aluminium about  $\frac{1}{100}$ th of a millimetre thick, and he found that from this window there proceeded in all directions rays which were deflected by a magnet, and which produced phosphorescence when they fell upon certain substances, notably upon tissue paper soaked in a solution of pentadecapentalolylketon. The very thin aluminium is difficult to get, and Mr. McClelland has found that if it is not necessary to maintain the vacuum for a long time, oiled silk answers admirably for a window. As the window is small the phosphorescent patch produced by it is not bright, so that I will show instead the other property of the cathode rays, that of carrying with them a negative charge. I will place this cylinder in front of the hole, connect it with the electrometer, turn on the rays, and you will see the cylinder gets a negative charge; indeed this charge is large enough to produce the well known negative figures when the rays fall on a piece of ebonite which is afterwards dusted with a mixture of red lead and sulphur.

From the experiments with the closed cylinder we have seen that when the negative rays come up to a surface even as thick as a millimetre, the opposite side of that surface acts like a cathode, and gives off the cathodic rays; and from this point of view we can understand the very interesting result of Lenard that the magnetic deflection of

the rays outside the tube is independent of the density and chemical composition of the gas outside the tube, though it varies very much with the pressure of the gas inside the tube. The cathode rays could be started by an electric impulse which would depend entirely on what was going on inside the tube; since the impulse is the same the momentum acquired by the particles outside would be the same; and as the curvature of the path only depends on the momentum, the path of these particles outside the tube would only depend on the state of affairs inside the tube.

The investigation by Lenard on the absorption of these rays shows that there is more in his experiment than is covered by this consideration. Lenard measured the distance these rays would have to travel before the intensity of the rays fell to one-half their original value. The results are given in the following table:—

Substance.	Coefficient of Absorption.	Density.	Absorption Density
Hydrogen (3 mm. press.) ..	0·00149	0·000000368	4040
„ (760) .. ..	0·476	0·0000484	5640
Air (0·760 mm. press.) ..	3·42	0·00123	2780
SO <sub>2</sub> .. ..	8·51	0·00271	3110
Collodion .. ..	3,310	1·1	3010
Glass .. ..	7,810	2·47	3160
Aluminium .. ..	7,150	2·70	2650
Silver .. ..	32,200	10·5	3070
Gold .. ..	53,600	19·3	2880

We see that though the densities and the coefficient of absorption vary enormously, yet the ratio of the two varies very little, and the results justify, I think, Lenard's conclusion that the distance through which these rays travel only depends on the density of the substance—that is, the mass of matter per unit volume, and not upon the nature of the matter.

These numbers raise a question which I have not yet touched upon, and that is the size of the carriers of the electric charge. Are they or are they not the dimensions of ordinary matter?

We see from Lenard's table that a cathode ray can travel through air at atmospheric pressure a distance of about half a centimetre before the brightness of the phosphorescence falls to about one-half of its original value. Now the mean free path of the molecule of air at this pressure is about  $10^{-5}$  cm., and if a molecule of air were projected it would lose half its momentum in a space comparable with the mean free path. Even if we suppose that it is not the same molecule that is carried, the effect of the obliquity of the collisions would reduce the momentum to one-half in a short multiple of that path.

Thus, from Lenard's experiments on the absorption of the rays outside the tube, it follows on the hypothesis that the cathode rays

are charged particles moving with high velocities, that the size of the carriers must be small compared with the dimensions of ordinary atoms or molecules. The assumption of a state of matter more finely subdivided than the atom of an element is a somewhat startling one; but a hypothesis that would involve somewhat similar consequences—viz. that the so-called elements are compounds of some primordial element—has been put forward from time to time by various chemists. Thus, Prout believed that the atoms of all the elements were built up of atoms of hydrogen, and Mr. Norman Lockyer has advanced weighty arguments, founded on spectroscopic consideration, in favour of the composite nature of the elements.

Let us trace the consequence of supposing that the atoms of the elements are aggregations of very small particles, all similar to each other; we shall call such particles corpuscles, so that the atoms of the ordinary elements are made up of corpuscles and holes, the holes being predominant. Let us suppose that at the cathode some of the molecules of the gas get split up into these corpuscles, and that these, charged with negative electricity and moving at a high velocity, form the cathode rays. The distance these rays would travel before losing a given fraction of their momentum would be proportional to the mean free path of the corpuscles. Now, the things these corpuscles strike against are other corpuscles, and not against the molecules as a whole; they are supposed to be able to thread their way between the interstices in the molecule. Thus the mean free path would be proportional to the number of these corpuscles; and, therefore, since each corpuscle has the same mass to the mass of unit volume—that is, to the density of the substance, whatever be its chemical nature or physical state. Thus the mean free path, and therefore the coefficient of absorption, would depend only on the density; this is precisely Lenard's result.

We see, too, on this hypothesis, why the magnetic deflection is the same inside the tube whatever be the nature of the gas, for the carriers of the charge are the corpuscles, and these are the same whatever gas be used. All the carriers may not be reduced to their lowest dimensions; some may be aggregates of two or more corpuscles; these would be differently deflected from the single corpuscle, thus we should get the magnetic spectrum.

I have endeavoured by the following method to get a measurement of the ratio of the mass of these corpuscles to the charge carried by them. A double cylinder with slits in it, such as that used in a former experiment, was placed in front of a cathode which was curved so as to focus to some extent the cathode rays on the slit; behind the slit, in the inner cylinder, a thermal junction was placed which covered the opening so that all the rays which entered the slit struck against the junction, the junction got heated, and knowing the thermal capacity of the junction, we could get the mechanical equivalent of the heat communicated to it. The deflection of the electrometer gave the charge which entered the cylinder.



Thus, if there are  $N$  particles entering the cylinder each with a charge  $e$ , and  $Q$  is the charge inside the cylinder,

$$N e = Q.$$

The kinetic energy of these

$$\frac{1}{2} N m v^2 = W$$

where  $W$  is the mechanical equivalent of the heat given to the thermal junction. By measuring the curvature of the rays for a magnetic field, we get

$$\frac{m}{e} v = I.$$

Thus

$$\frac{m}{e} = \frac{1}{2} \frac{Q I^2}{W}.$$

In an experiment made at a very low pressure, when the rays were kept on for about one second, the charge was sufficient to raise a capacity of 1.5 microfarads to a potential of 16 volts. Thus

$$Q = 2.4 \times 10^{-6}.$$

The temperature of the thermo junction, whose thermal capacity was 0.005 was raised  $3.3^\circ \text{C}$ . by the impact of the rays, thus

$$\begin{aligned} W &= 3.3 \times 0.005 \times 4.2 \times 10^7 \\ &= 6.3 \times 10^5. \end{aligned}$$

The value of  $I$  was 280, thus

$$\frac{m}{e} = 1.6 \times 10^{-7}.$$

This is very small compared with the value  $10^{-4}$  for the ratio of the mass of an atom of hydrogen to the charge carried by it. If the result stood by itself we might think that it was probable that  $e$  was greater than the atomic charge of atom rather than that  $m$  was less than the mass of a hydrogen atom. Taken, however, in conjunction with Lenard's results for the absorption of the cathode rays, these numbers seem to favour the hypothesis that the carriers of the charges are smaller than the atoms of hydrogen.

It is interesting to notice that the value of  $e/m$ , which we have found from the cathode rays, is of the same order as the value  $10^{-7}$  deduced by Zeeman from his experiments on the effect of a magnetic field on the period of the sodium light.

[J. J. T.]

Friday, May 21, 1897.

SIR EDWARD FRANKLAND, K.C.B. D.C.L. LL.D. F.R.S.  
Vice-President, in the Chair.

THE RIGHT HON. LORD KELVIN, G.C.V.O. D.C.L. LL.D. F.R.S. M.R.I.

*Contact Electricity of Metals.*

§ 1. WITHOUT preface two 95 years old experiments of Volta's were, one of them shown, and the other described. The apparatus used consists of : (a) a Volta-condenser of two varnished brass plates, of which the lower plate is insulated in connection with the gold leaves of a gold leaf electroscope, and the upper plate is connected by a flexible wire with the sole plate of the instrument; (b) two circular discs, one of copper and the other of zinc, each polished and unvarnished. I hold one in my right hand by a varnished glass stem attached to it, while on my left hand I hold the other, which is kept metallically connected with the sole plate of the electroscope by a thin flexible wire.

To commence the experiment I place one disc resting on the other, and lift the two till the upper touches a brass knob connected by a stiff metal wire with the lower plate of the Volta condenser. I break this contact and then lift the upper plate of the condenser; you see no divergence of the gold leaves. This proves that no disturbing electric influence sufficient to show any perceptible effect on our gold leaf electroscope is present. Now I repeat what I did, with only this

change—I hold the lower disc with the upper disc resting on it two or three centimetres below the knob. I then with my right hand lift the upper plate of the Volta-condenser; you see a very slight divergence between the shadows of the gold leaves on the screen. I can just see it by looking direct at the leaves from a distance of about half a metre. Still holding the lower plate firmly in my left hand in the same position, and holding the upper plate by the top of its glass stem in my right, at first resting on the lower plate I lift it and

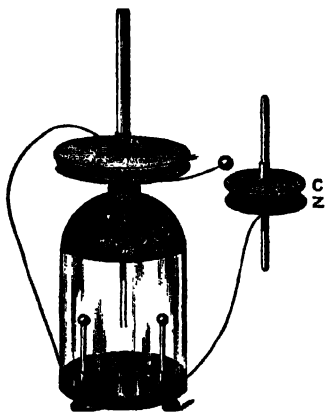


FIG. 1.

let it down very rapidly a hundred times, so as to produce one hundred cycles of operation—break contact between discs, make and break contact between upper disc and knob, make contact between discs. Lastly, I lift the upper plate of the condenser; you see now a great divergence of the gold leaves, many of you can see it direct on the leaves, while all of you can see it by their shadows on the screen. Now, keeping the upper plate of the condenser still unmoved, I bring a stick of rubbed sealing-wax into the neighbourhood of the electroscope; you see the divergence of the leaves is increased. I remove the sealing-wax and the divergence diminishes to what it was before. This proves that the gold leaves diverge in virtue of resinous electricity upon them, and therefore that the insulated plate of the condenser received resinous electricity from the copper disc. If now I interchange the two discs so that the upper is zinc and the lower copper, and repeat the experiment, you see that the rubbed sealing-wax diminishes the divergence as it is brought from a distance into the neighbourhood, and that a glass rod rubbed with silk increases the divergence. Hence we conclude that in the separation of two discs of copper and zinc the copper carries away resinous electricity and the zinc vitreous electricity.

§ 2. Experiment 2.—The same apparatus as in Experiment 1, except that the polished zinc and copper discs have their opposed faces varnished with shellac, and are provided with wires soldered to them for making metallic connection between them when the upper rests on the lower, as shown in Fig. 2. All operations are the same as in Experiment 1, but now with this addition—when the upper disc rests on the lower, make and break metallic contact by hand as shown in the diagram. The results are the same as those of Experiment 1, except that the quantity of electrification given to the gold leaves by a single cycle of operations is generally greater than in Experiment 1, for this reason: In Experiment 1 at the instant of breaking contact between the zinc and copper there is generally some degree of inclination between the two discs, while at the corresponding instant of Experiment 2 they are parallel and only separated by the insulating coats of varnish. If great care is taken to keep the discs as nearly as possible parallel at the instant of separation, the effect of a single separation may be made greater in Experiment 1 than in Experiment 2 (see § 3 below).

§ 3. An instructive variation of Experiment 1 may be made by giving a large inclination,  $5^\circ$ , or  $10^\circ$ , or  $20^\circ$ , of the upper plate to the lower, while still in contact and at the instant of separation. By operating thus the experiment may be made to fail so nearly completely that no divergence of the leaves will be observed even after one hundred cycles.

§ 4. These two experiments, with the variation described in § 3, put it beyond all doubt that Volta's electromotive force of contact between two dissimilar metals is a true discovery. It seems to have been made by him about the year 1801; at all events he exhibited

his experiments, proving it in that year to a Commission of the French Institute (Academy of Sciences). It is quite marvellous that the fundamental experiment (§ 1 above), simple, easy and sure as it is,\* is not generally shown in courses of lectures on electricity to students, and has not been even mentioned or referred to in any English text-book later than 1845, or at all events not in any one

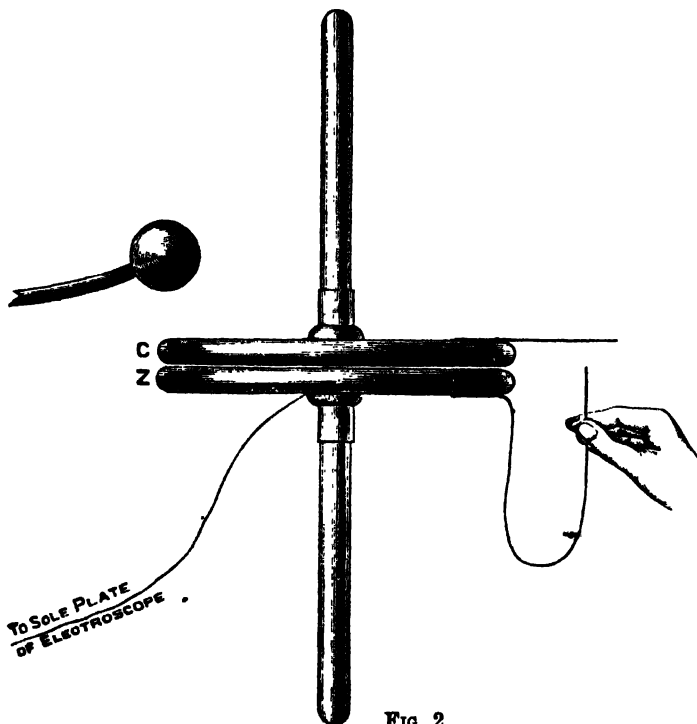


FIG. 2.

of a large number in which I have looked for it, except in the 'Elementary Treatise on Electricity and Magnetism,' founded on Joubert's '*Traité Élémentaire d'Électricité*,' by Foster and Atkinson, 1896 (p. 136). The only other places in which I have seen it described in the English language are Roget's article in the '*Encyclopædia Metropolitana*' referred to above; Tait's '*Recent Advances in Physical Science*,' 1876; and Professor Oliver Lodge's most valuable, interesting and useful account of all that had been done for knowledge of contact electricity from its discovery by Volta till 1884, in his Report

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\* Fully and clearly described in Roget's article on "Galvanism," in the '*Encyclopædia Metropolitana*,' vol. iv. edition 1845, p. 210.

to the British Association of that year, 'On the Seat of the Electromotive Forces in the Voltaic Cell.'

§ 5. The reason for this unmerited neglect of a great discovery regarding properties of matter is that it was overshadowed by an earlier and greater discovery of its author, by which he was led to the invention of the voltaic pile and crown of cups, or voltaic battery, or, as it is sometimes called, the galvanic battery. Knowing, as we now know, both Volta's discoveries, we may describe the earlier most shortly by saying that the simple experiment (§ 1 above), demonstrating the later discovery, is liable to fail if a drop of water is placed on the lower of the two polished plates. It fails if (see Fig. 4 below) the last connection between the zinc and copper, when the upper disc is lifted, is by water. It would not fail (see Fig. 6 below) nor be sensibly altered from what is found with the dry polished metals, if the upper disc is slightly tilted in the lifting, so as to break the water arc before the separation between the metals, and secure that the last connection is contact of dry metals. To show this to you more readily than by a Volta condenser with gold leaf electroscope, I shall now use instead my quadrant electrometer without condenser.

(1) Holding the copper disc connected with the metal case of the electrometer in one hand, with my other hand I hold by a glass handle the zinc disc, which you see is connected by a fine wire with the insulated quadrants of the electrometer. I first place the zinc resting on the copper, both being polished and dry. You now see the spot of light at the point marked O on the scale, which I call the metallic zero. I now lift the zinc disc two or three millimetres from resting on the copper, and you see the spot of light travelling largely to the right, which proves that vitreous electricity has passed from the zinc disc through the connecting wire to the insulated quadrants of the electrometer. I lower the zinc disc down to rest again on the copper disc; you see the spot of light again comes back to the metallic zero.

(2) I now raise the zinc disc, and with a little piece of wet wood (or a quill pen) place a little mound of water on the copper disc, as shown in Fig. 3. I bring down the zinc disc to touch the top of the

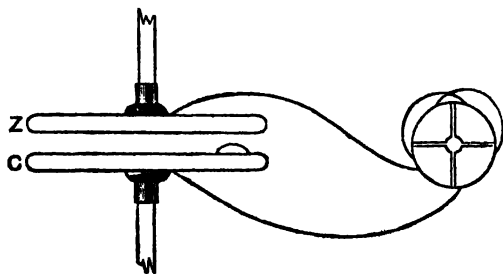


FIG. 3.

little mound of water, keeping it parallel to the copper disc so that there is no metallic contact between them (Fig. 4); you see that the

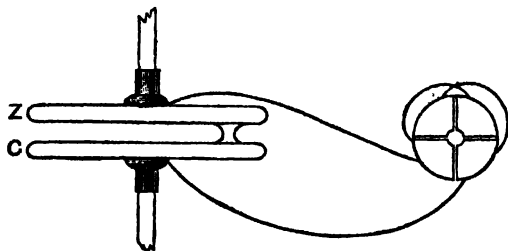


FIG. 4.

spot of light moves to the left and settles at a point marked E (which I call the electrolytic zero of our circumstances), a few scale divisions to the left of the metallic zero. This motion and settlement is the simplest modern exhibition of Volta's greatest discovery.

(3) Now that the spot of light has settled, I lift the zinc disc a millimetre till the water column is broken, and then two or three centimetres farther (Fig. 5); the spot of light does not move, it

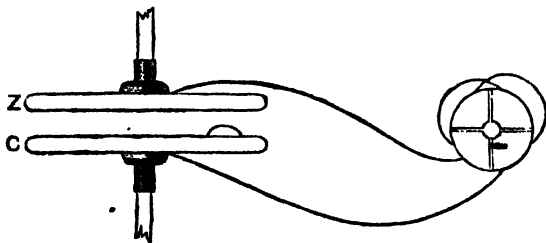


FIG. 5.

remains at E. I lower the zinc disc again: still no motion of the spot of light, not even when the zinc again touches the little mound of water.

(4) Now I tilt the zinc disc slightly till it makes a dry metallic contact with the copper, as shown in Fig. 6; while the water arc still

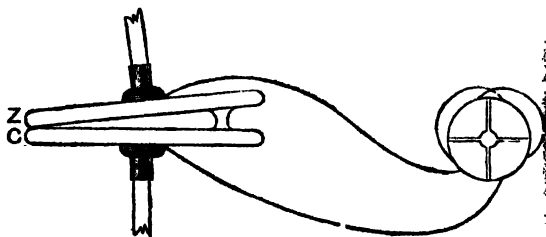


FIG. 6.

remains unbroken. You see the spot of light, at the instant of metallic contact, suddenly leaves E and moves to the right, and settles quickly at the metallic zero after a few vibrations through diminishing range.

(5) Lastly, I break the metallic contact, and hold the zinc disc again parallel to the copper (Fig. 4) with the water connection still remaining unbroken between them; the spot of light shows no sudden motion; it creeps to the left till, in half a minute or three-quarters of a minute, it reaches its previous steady position on the left. This is the now well-known phenomenon (never known to Volta) of the recovery of a voltaic cell from electrolytic polarisation after a metallic short-circuit.

§ 6. The succession of experiments described in § 5, interpreted according to elementary electrostatic law, proves the following conclusions:—

(1) When the dry and polished discs of zinc and copper are metallically connected and held parallel, their opposed faces are oppositely electrified, the zinc with vitreous electricity, and the copper with resinous electricity, in quantities varying inversely as the distance between them when this is small in comparison with the diameter of each.

(2) The opposed polished faces are non-electrified when polished portions of the zinc and copper surfaces are connected by water, and when there is no metallic connection between them. Or, if not absolutely free from electrification, they may be found slightly electrified, zinc resinously or vitreously, and copper vitreously or resinously, according to differences in respect to cleanness, polish, or scratching or burnishing, as explained in § 16 below; and according to polarisation or other difference in the wetted portions of the surfaces.

If instead of pure water we take a weak solution of common salt, or carbonate of soda, or sulphate of zinc or ammonia, we find results but little affected by the differences of the liquids.

§ 7. But if the polished surface of either the copper or the zinc is oxidised, or tarnished in any way, notably different results are found when the experiments of § 5 are repeated with the disc or discs thus altered.

For example, hold the copper disc, with its polished side up, over a slab of hot iron, or a spirit lamp, or a Bunsen burner, till you see a perceptible change of colour, due to oxidation of the previously polished face. Then allow the copper to cool, and repolish a small area near one edge; place a little mound of water upon this area, and operate as in § 5 (2), (3). The water connection between polished zinc and polished copper brings the spot of light to the same electrolytic zero E as before. But now, when we lift the zinc disc and break the water connection, the spot of light moves to the right, instead of remaining steady as it does when both the dry opposed surfaces are polished. If

next we tarnish the zinc disc by heat, as we did for the copper disc, and repeat the experiment with wholly polished copper, and with the zinc disc oxidised where dry, and polished only where wet by the water connection, we find still the same electrolytic zero E; but now the spot of light moves to the left when we lift the zinc disc and break the water connection.

§ 8. The experiments of § 7, interpreted in connection with those of § 5, prove that there are dry contact voltaic actions between metallic copper and oxide of copper in contact with it, and between metallic zinc and oxide of zinc in contact with it; according to which, dry oxide of copper is resinous to copper in contact with it, and dry oxide of zinc is resinous to zinc in contact with it, just as copper is resinous to zinc in contact with it. We may verify this conclusion by another interesting experiment. Taking, for instance, the oxidised copper plate, with a little area polished for contacts; put a little mound of copper, instead of the mound of water, on this area for contact with the upper plate; and for the upper plate take polished copper instead of polished zinc. If we operate now as in § 7, the spot of light settles at the metallic zero O when the metallic contact is made, instead of at the electrolytic zero E, as it did when we had water connection between zinc and copper. But now, just as in § 7, the spot of light moves to the right when the contact is broken and the upper plate lifted, which proves that vitreous electricity flows into the electrometer from the upper plate, when its distance from the lower plate is increased after breaking the metallic contact. We conclude that when the two plates were parallel, and very near one another, and when there was metallic connection between them, vitreous and resinous electricities were induced upon the opposed surfaces of metallic copper and oxidised copper respectively. This statement, which we know from § 7 to be also true for zinc compared with oxidised zinc, is probably also true for every oxidisable metal compared with any one of its possible oxides. It is true, as we shall see later (appended paper of 1880-81; also Erskine Murray's paper referred to in § 15), even for platinum in its ordinary condition in our atmosphere of 21 per cent. oxygen and 79 per cent. nitrogen, voltaically tested in comparison with platinum which has been recently kept for several minutes or several hours in an atmosphere of pure oxygen, or even in an atmosphere of 95 per cent. oxygen and 5 per cent. nitrogen.

§ 9. Hitherto we have had no means of measuring the amount of the Volta-contact electric force between dry metals, except observation of the degrees of deflection of the gold leaves of an electroscope, or of the spot of light of the quadrant electrometer consequent upon operations performed upon different pairs of metals, with dimensions and distances of motion exactly the same, and comparison of these deflections with the steady deflection from the metallic zero given by polished zinc and copper connected conductively with one another by water, and connected metallically with the two electrodes of an



electroscope or electrometer. Kohlrausch, in 1851,\* devised an apparatus for carrying out this kind of investigation systematically, and with a good approach to accuracy, by aid of a Dellman's electrometer and a Daniell's cell, as more definite and constant than a zinc-water-copper cell. This method of Kohlrausch's for measuring the Volta electromotive forces between dry metals, "has been employed with modifications by Hankel, by Gerland, by Clifton, by Ayrton and Perry, by von Zahn, and by most other experimenters on the subject."† About thirty-seven years ago, in repetitions of Volta's fundamental experiment proving contact electricity by electroscopic phenomena resulting from change of distance between parallel plates of zinc and copper, I found a null method for measuring electromotive forces due to metallic contact between dissimilar metals, in terms of the electromotive force of a Daniell's cell, which is represented diagrammatically in Fig. 7, and in perspective in Fig. 8. The two discs are protected against disturbing influences by a metal sheath. The lower disc is permanently insulated in a fixed position, and is kept connected with the insulated pair of quadrants of a quadrant electrometer. The upper disc is supported by a metal stem passing through a collar in the top of the sheath, so that it is kept always parallel to the lower disc and metallically connected to the sheath, while it can be lifted a few centimetres at pleasure from an adjustable lowest position in which its lower face is about half a millimetre or a millimetre above the upper face of the lower disc. A portion of the wire connecting the lower plate to the insulated quadrants of the electrometer is of polished platinum, and contact between this and a platinum-tipped wire connected to the slider of a potential divider is made and broken at pleasure. For certainty of obtaining good results it is necessary that these contacts should be between clean and dry polished metals, because if the last connection on breaking contact is through semi-moist dust, or oxide, or "dirt" (defined by Lord Palmerston to be matter in a wrong place), or if it is anything other than metallic, vitiating disturbance is produced.

§ 10. To make an experiment, first test the insulation with the upper plate held up in its highest position, and after that with it let down to its lowest position, in each case proceeding thus: Holding by hand the wire connected to the slider, run the slider to zero, make contact at P, observe on the screen the position of the spot of light from the electrometer mirror for the metallic zero, and then run the slider slowly to the top of its scale and break contact; the spot of light should remain steady, or at all events should not lose more than a very small percentage of its distance from metallic zero, in half a

\* 'Poggendorff Annalen,' vols. lxxv. p. 88; lxxxii. pp. 1 and 45; and lxxxviii. p. 465, 1851 and 1853.

† Prof. O. J. Lodge, 'On the Seat of the Electromotive Forces in the Voltaic Cell,' Brit. Ass. Report, 1884, pp. 464-529.

minute. Repeat the test with the cell reversed. If the test is satisfactory with the upper plate high, the insulation of the insulated quadrants in the electrometer and of the lower disc in the Volta-condenser is proved good. If after that the test is not satisfactory with the upper disc at its lowest, we infer that there are vitiating shreds between the two plates, and we must do what we can to remove them; or, if necessary, we must alter the screw-stop at the top so as to increase the shortest distance between the plates sufficiently to prevent bridges of shred or dust between them, and so to give good insulation. The smaller we make the shortest distance with perfect

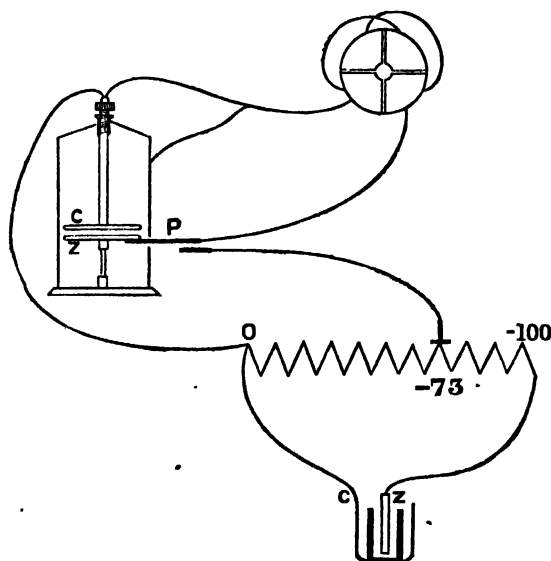


FIG. 7.

enough insulation, the more sensitive is the apparatus for the measurement of contact electricity performed as follows.

§ 11. Run the slider to zero; make and keep made the contact at P till the spot of light settles at the metallic zero; break contact at P, and lift the upper plate slightly. (If you lift it too far, the spot of light may fly out of range.) If the spot of light moves in the direction showing positive electricity on the insulated quadrants (as it does if the lower plate is zinc and the upper copper), connect the cell to make the slider negative (as shown in Fig. 7). Repeat the experiment with the slider at different points on the scale, until you find that, with contact P broken, lifting the upper plate causes no motion of the spot of light. If the compensating action with the slider at the top

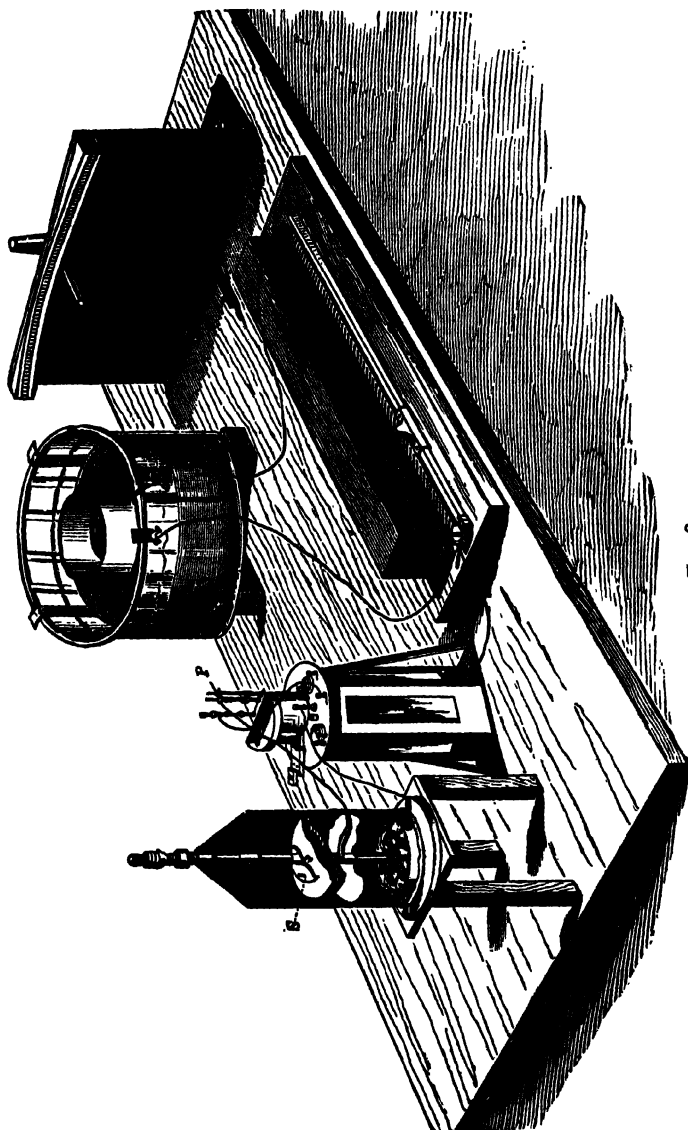


FIG. 8.

of the range is insufficient, add a second cell; if it is still insufficient, add a third cell; if still insufficient, add a fourth.\*

§ 12. By this method I made an extended series of experiments in the years 1859-61, as stated in a short paper communicated to Section A of the British Association at its Swansea meeting in August 1880, which with additions published in 'Nature' for April 14, 1881, is appended to the present article.

§ 13. Quite independently,† Mr. H. Pellat found the same method, and made admirable use of it in a series of experiments described in theses presented to the Faculty of Sciences in Paris in 1881,‡ of which the results, accurate to a degree of minuteness unknown in previously published researches on the electrical effects of dry contacts between metals, constitute in many respects the most important and most interesting extension of our knowledge of contact electricity since the times of Volta and Pfaff. One of his results (I shall have to speak of others later) was that Pfaff was right in 1829§ when he described experiments in which he found no difference in the Volta-contact-electromotive force between zinc and copper, whether tested in dry or damp air, oxygen, nitrogen, hydrogen, carburetted hydrogen, or carbonic acid, so long as no visible chemical action occurred; and that De la Rive was not right when he "asserted that there was no Volta effect in the slightly rarefied air then known as vacuum."|| Pfaff experimented with varnished plates; Pellat arrived at the same conclusion with polished unvarnished plates of zinc and copper. He found slight variations of the Volta electromotive force due to the nature of the gas surrounding the plates, and to differences of its pressure, of which he says: "Ces variations sont très faibles, par rapport à la différence de potentiel totale. . . . Ces variations dans la différence de potentiel sont toujours en retard sur les changements de pression. Elles ne paraissent donc pas dépendre directement de celle-ci, mais bien des modifications qui en résultent dans la nature

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\* The only case hitherto tested by any experimenter, so far as known to me, in which more than two Daniell cells would be required for the compensation, is bright metallic sodium, guarded against oxide by glass, in Mr. Erskine Murray's experiments (§ 18 below), showing volta-difference of 3.56 volts from his standard gold plate. For direct test this would require four Daniell cells on the potential divider. The greatest volta-difference of potentials observed by Pellat was 1.08 volts, for which a Daniell's cell would rather more than suffice. About 1862 I found considerably more than the electromotive force of a single Daniell's element required to compensate the Volta electromotive force between polished zinc and copper oxidised by heat to a dark purple or slate colour.

† Ann. de Chimie et de Physique, vol. xxiv. 1881, p. 20, footnote.

‡ 'Thèses présentées à la Faculté des Sciences de Paris, pour obtenir le Grade de Docteur-ès-Sciences Physiques,' par M. H. Pellat, Professeur de Physique au Lycée Louis le Grand, No. 461, juin 22, 1881. See also 'Journal de Physique,' 1881, xvi. p. 68, and May 1880, 'Différence de potentiel des couches électriques qui recouvrent deux métaux en contact.'

§ Ann. de Chim., 2 series, vol. xli. p. 236.

|| Lodge, Brit. Assoc. Report, 1884, pp. 477-8.

de la surface métallique, modifications qui mettent un certain temps à se produire." The smallest pressures for which Pellat made his experiments were from 8 to 4 or 5 cm. of mercury.\*

§ 14. The same method was used by Mr. J. T. Bottomley in an investigation by which he demonstrated with minute accuracy the equality of the Volta-contact-difference measured in a glass tube exhausted to less than  $\frac{1}{13}$  mm. of mercury\* ( $2\frac{1}{2}$  millionths of an atmosphere), and immediately after in the same tube filled with air to ordinary atmospheric pressure; and again exhausted and filled with hydrogen to atmospheric pressure three times in succession; and again exhausted and filled to atmospheric pressure with oxygen. In some cases the electrical test was repeated several times, while the gas was entering slowly. The actual apparatus which he used is before you, and in it I think you will see with interest the little Volta-condenser, with plates of zinc and copper a little larger than a shilling, the upper hung on a spiral wire by a long hook carrying also a small globe of soft iron. Thus you see by aid of an external magnet I can lift and lower the upper plate without moving the vacuum tube which, during the experiments, was kept in connection with a Sprengel pump and phosphoric acid drying tubes. Mr. Bottomley sums up thus: "The result of my investigation, so far as it has gone, is that the Volta contact effect, so long as the plates are clean, is exactly the same in common air, in a high vacuum, in hydrogen at small and full pressure, and in oxygen. My apparatus, and the method of working during these experiments, was so sensitive that I should certainly have detected a variation of 1 per cent. in the value of the Volta contact effect, if such a variation had presented itself."†

§ 15. With the same method further researches have been carried on by Mr. Erskine Murray, and important and interesting results obtained, within the last four years, in the Physical Laboratories of the Universities of Glasgow and Cambridge. He promises a paper for early communication to the Royal Society, and, from a partial copy of it which he has already given me, I am able to tell you of some of his results. Taking generally as standard a gilt brass disc which he found among the apparatus remaining from my experiments of 1859-61, he measured Volta-differences from it in terms of the modern standard *one volt*. These differences are what we may call the Volta-potentials of the different metallic surfaces, or surfaces of metallic oxides, iodides, &c., or metallic surfaces altered by cohesion to them of gases or vapours, or residues of liquids which had been used for washing them; if for simplicity we agree to call the Volta-potential of the gold, zero. As a rule he began each experiment by

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\* A very high exhaustion had been maintained for two days, and finally perfected by two and a half hours' working at the pump immediately before the electric testing experiment.

† Brit. Assoc. Report, 1885, pp. 901-3.

polishing the metal plate to be tested on clean glass paper or emery cloth, and then measured its difference of potential from the standard gold plate. After that the plate was subjected to some particular treatment, such as filing or burnishing; or polishing on leather or paper; or washing with water, or alcohol, or turpentine, and leaving it wet or drying it; or heating it in air, or exposing it to steam or oxygen, or fumes of iodine or sulphuretted hydrogen; or simply leaving it for some time under the influence of the atmosphere. The plate as altered by any of these processes was then measured for potential against the standard gold. Very interesting and instructive results were found; only of one can I speak at present. Burnishing by rubbing it firmly with a rounded steel tool, or by rubbing two plates of the same metal together, increased the potential in every case; that is to say made the metallic surface more positive if it was positive to begin with; or made it less negative or changed it from negative to positive, if it was negative to begin with. Thus:—

Zinc immediately after being scratched sharply by polishing on clean glass paper was found	+	·70 volt.
After being burnished with hard steel burnisher it was found	+	·94 volt.
After being left to itself for 2 hours it was found	+	·92 volt.
After further burnishing	+	1·00 volt.
After still further burnishing	+	1·02 volt.
It was then scratched by polishing on glass paper, and its surface potential returned to its original value of	+	·70 volt.

§ 16. This seems to me a most important result. It cannot be due to the removal of oxygen, or oxide, or of any other substance from the zinc. It demonstrates that change of arrangement of the molecules at the free surface, such as is produced by crushing them together, as it were, by the burnisher, affects the electric action between the outer surface of the zinc and the opposed parallel gold plate. It shows that the potential \* in zinc (uniform throughout the homogeneous interior)

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\* There has been much of wordy warfare regarding potential in a metal, but none of the combatants has ever told what he means by the expression. In fact the only definition of electric potential hitherto given has been for vacuum, or air, or other fluid insulator. Conceivable molecular theories of electricity within a solid or liquid conductor might admit the term potential at a point in the interior; but the function so called would vary excessively in intermolecular space, and must have a definite value for every point, whether of intermolecular space or within the volume of a molecule, or within the volume of an atom, if the atom occupies space. It would also vary intensely from point to point in the ether or air outside the metal at distances from the frontier small or moderate in comparison with the distance from molecule to molecule in the metal.

But when, setting aside our mental microscopical binocular which shows us atoms and molecules, we deal with the mathematical theory of equilibrium and motion of electricity through metals with outer surfaces bounded by ether or air or other

increases from the interior through the thin surface layer of a portion of its surface affected by the crushing of the burnisher, more by  $\cdot 32$  volt than through any thin surface-layer of portions of its surface left as polished and scratched by glass paper. The difference of potentials of copper and zinc across an interface of contact between them is only about  $2\frac{1}{2}$  times the difference of potential thus proved to be produced between the homogeneous interior of the zinc and its free surface, by the burnishing. Pellat had found that polished metallic surfaces, seemingly clean and free from visible contamination of any kind, became more positive by rubbing them forcibly with emery paper, zinc showing the greatest effect, which was  $\cdot 23$  volt. Murray's burnished surface of zinc actually fell  $\cdot 32$  volt when scratched by polishing on glass paper.

§ 17. With two copper plates (a), (b) polished on emery and each compared with standard gold, Murray found. . . . . (a) —  $\cdot 11$  volt.  
 (b) —  $\cdot 06$  volt.

They were then burnished by rubbing them forcibly together, and again tested separately; he found . . . . . (a) —  $\cdot 02$  volt.  
 (b) —  $\cdot 02$  volt.

Rises of Volta-potential of about the same amount were produced by burnishing with a steel burnisher copper plates which had been polished and scratched in various ways. Such experiments as those of Murray with burnishing ought to be repeated with hammering or crushing by a Bramah's press. Indeed Pellat\* suggested that metals treated bodily "par le laminage ou le martelage" (rolling or hammering) might probably show Volta-electric properties of the same kind as, but more permanent than, those which he had found to be produced by violent scratching with emery paper.

§ 18. It is interesting to remark that Murray's most highly burnished zinc differed from his emery-polished copper (a) by  $1\cdot 13$

insulating fluids or solids, we find it convenient to use a mathematical function of position called potential in the interior of each metal. This function must, for the case of equilibrium, fulfil the condition that it is of uniform value through each homogeneous portion of metal. Its value must, as a rule, change gradually (or abruptly) with every gradual (or abrupt) change of quality of substance occupying space.

To illustrate the difficulty and complexity of expression with which I have struggled, and to justify if possible my ungainly resulting sentence in the text, consider the case of a crystal of pure metal: suppose, for example, an octahedron with truncated corners, all natural faces and facets. In all probability Volta-differences of potential would be found between the octahedral and truncational faces. We might arbitrarily define the uniform interior potential as the potential of the air either near an octahedral face or near a truncational face; or, still arbitrarily, we might define it as some convenient mean or average related to measurements of Volta-differences of potential between the different faces.

\* Ann. de Chimie et de Physique, 1881, vol. xxiv. footnote on p. 83.

volts. This is considerably greater, I believe, than the highest hitherto recorded Volta-difference between pure metallic surfaces of zinc and copper.

By far the greatest Volta-difference between two metallic surfaces hitherto measured is, I believe, 8.56 volts, which Murray, in another part of his work, found as the Volta-difference between bright sodium protected by glass and his standard gold. He had previously found a copper surface after exposure to iodine vapour to be  $-.84$  relatively to his standard gold. The difference between this iodised surface and the bright metallic surface of sodium was therefore 8.90 volts: which is the highest dry Volta electromotive force hitherto known.

§ 19. Seebeck's great discovery of thermoelectricity (1821) was a very important illustration and extension of the twenty years' earlier discovery of the contact electricity of dry metals by Volta. It proved independently of all disturbing conditions that the difference of potentials between two metals in contact varies with the temperature of the junction. Thus, for instance, in the copper-iron arrangement

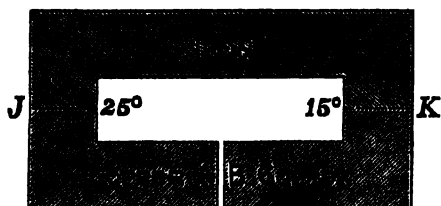


FIG. 9.

represented in Fig. 9, with its hot junction at  $25^{\circ}$  and its cold at  $15^{\circ}$ , the electromotive force tends to produce current from copper to iron through hot, and its amount is .00148 volt: that is to say, if the circuit is broken at A B the two opposed faces A, B, at equal temperatures, present a difference of electric potential of .00148 volt, with B positive relatively to A. This is not too small a difference to be tested directly by the Volta-static method, worked by two exactly similar metal discs connected to A and B, when they are at their shortest distance from one another, and then disconnected from A and B, and separated and tested by connection with a delicate quadrant electrometer. But the test would be difficult, because of the difficulty of preparing the opposed surfaces of two equal and similar discs, so as to make them equal in their surface-Volta-potentials within one one-thousandth of a volt, or even to make their difference of potentials constant during the time of experiment within one one-thousandth of a volt. There would, however, be no interest in making the experiment in this way, because by the electromagnetic method we can with ease exhibit and measure with great accuracy the difference of potentials between A and B, by keeping them exactly at one tempe-



perature and connecting them by wires of any kind with brass or other terminals of a galvanometer of high enough resistance not to sensibly diminish the difference of potentials between A and B, provided all the connections between metals of different quality except J and K are kept at one and the same temperature (or pairs of them, properly chosen, kept at equal temperatures).

§ 20. Suppose, now, instead of breaking a circuit of two metals at a place in one of the metals, as A B in copper in Fig. 9, we break it at one of the junctions between the two metals, as at C' C, I' I, Fig. 10. C D represents a movable slab of copper which (for § 22 below) may be pushed in so as to be wholly opposite to I' I, or at pleasure drawn out to any position, still resting on the copper below it as shown in the diagram. Calling zero the uniform potential over the surfaces C' C D, the potential at I' I would be about  $+ \cdot 16$  volt (according to

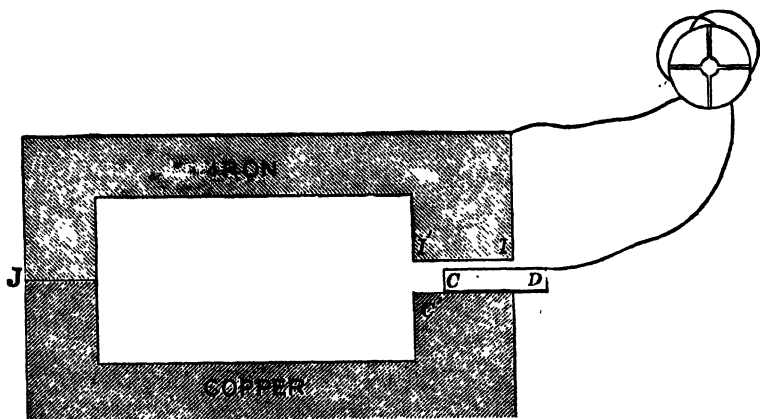


FIG. 10.

Murray's results for emery-polished copper and iron surfaces) if the temperature at J and throughout the system is uniform at about  $15^{\circ}$  C. Keeping now the temperature of C' C, I' I exactly at  $15^{\circ}$ , let the temperature of J be raised to  $25^{\circ}$ . The difference of potentials between C' C and I' I would be increased to  $\cdot 16148$  volt, supposing  $\cdot 16000$  to have been exactly the difference of potentials when the temperature of J was  $15^{\circ}$ . This difference of differences of potentials would be just perceptible on the most delicate quadrant electrometer connected as indicated in the diagram. Lastly, raise the temperature of C' C and I' I to exactly  $25^{\circ}$ , J being still kept at this temperature: the spot of light of the electrometer will return exactly to its metallic zero. But, would the Volta-difference of potentials between the surfaces C' C; I' I remain unchanged, or would it return exactly to its previous value of  $\cdot 16000$ , or would it come to some other value? We cannot answer this question without experiment. The

proper method, of course, would be to use the metal-sheathed Volta-condenser and compensation (§ 9 above), and with it measure the Volta-differences between copper and iron at different temperatures, the same for the two metals in each case. The sheath and everything in it should, in each experiment, be kept at one and the same constant temperature. But it would probably be very difficult to get a decisive answer, because of the uncertainties and time-lags of changes in the Volta-potential of metallic surfaces with change of temperature, which, if we may judge from Pellat's and Murray's experiments on effects of temperature when the two metals are unequally heated, would probably also be found when the temperatures of the two metals, kept exactly equal, are raised or lowered at the same time.

§ 21. The thermoelectric difference between bismuth and antimony is about ten times that between copper and iron for temperature differences of ten or twenty degrees on the two sides of  $20^{\circ}\text{C}$ , and their Volta-contact difference is exceedingly small (according to Pellat, just one one-hundredth of a volt when both their surfaces are strongly scratched by rubbing with emery). It would be very interesting, and probably instructive, to find how much their Volta-contact difference varies with temperature by the method at present suggested. The great variations of Volta-surface potentials, found by Pellat and Murray, when one of the two metals is heated, may have been due to difference of temperatures between the two opposed plates with air between them; and it is possible that no such large variation, or that large variation only due to changes of cohering gases, may be found when the two metals are kept at equal temperatures, and these temperatures are varied as in the experiment I am now suggesting.

§ 22. Peltier's admirable discovery (1834) of cold produced where an electric current crosses from bismuth to antimony, and heat where it crosses from antimony to bismuth, in a circuit of the two metals, with a current maintained through it by an independent electromotive force, is highly important in theory, or in attempts for theory, of the contact electricity of metals.

From an unsatisfactory \* hypothetical application of Carnot's principle to the thermodynamics of thermoelectric currents I long ago inferred † that probably electricity crossing a contact between copper and iron in the direction from copper to iron would produce cold, and in the contrary direction heat when the temperature is below  $280^{\circ}\text{C}$ . (the thermoelectric neutral temperature of copper and iron),‡ and I verified this conclusion by experiment.§

\* 'Mathematical and Physical Papers,' vol. i. art. xlviii. § 106, reprinted from 'Transactions of the Royal Society of Edinburgh,' May 1854.

† Ibid. § 116 (19).

‡ In a thermoelectric circuit of copper and iron the current is from copper to iron through hot when both junctions are below  $280^{\circ}\text{C}$ . It is from iron to copper through hot when both junctions are above  $280^{\circ}\text{C}$ .

§ 'Experimental Researches in Thermoelectricity,' Proc. R. S. May 1854; republished as art. li. in 'Mathematical and Physical Papers,' vol. i. (pp. 464-465).

Hence we see, looking to Fig. 10, if the movable copper plate CD is allowed to move inwards (in the position shown in the diagram it is pulled inwards by the Volta-electrifications of the opposed surfaces of iron and copper), cold will be produced at the junction J, all the metal being at one temperature to begin with; and if we draw out the copper plate CD, heat will be produced at J. The thermodynamics of this action,\* because it does not involve unequal temperatures in different parts of the metals concerned, is a proper subject for unqualified application of Carnot's law, and has nothing of the unsatisfactoriness of the thermodynamics of thermoelectric currents, which essentially involves dissipation of energy by conduction of heat through metals at different temperatures in different parts. At present we cannot enter further into thermodynamics than to remark that when the plate CD is drawn out, the heat produced at J is not the thermal equivalent of the work done by the drawing out of the copper plate, but in all probability is very much less than the thermal equivalent. Probably by far the greater part of the work spent in drawing out the plate against the electric attraction goes to storing up electrostatic energy, and but a small part of it is spent on heat produced at J; or on excess (positive or negative) of this Peltier heat above quasi-Peltier (positive or negative) absorptions of heat in the surface layers of the opposed surfaces when experiencing changes of electrification.

§ 23. Returning to Fig. 9; suppose, by electrodes connected to A B and an independent electromotive force, a current is kept flowing from copper to iron through one junction; and from iron to copper through the other; the Peltier heat produced where the current passes from iron to copper is manifestly not the thermal equivalent of the work done. In fact, if the two junctions be at equal temperatures the amounts of Peltier heat produced and absorbed at the two junctions will be equal, and the work done by the independent electromotive force will be spent solely in the frictional generation of heat.

§ 24. Many recent writers,† overlooking the obvious principles of §§ 22, 23, have assumed that the Peltier evolution of heat is the thermal equivalent of electromotive force at the junction. And in consequence much confusion, in respect to Volta's contact electricity and its relation to thermoelectric currents, has largely clouded the views

\* [March, 1898.] It has been given in a communication to the Royal Society of Edinburgh entitled 'The Thermodynamics of Volta-contact Electricity'; Feb. 21, 1898.

† Perhaps following Clerk Maxwell, or perhaps independently. At all events we find the following in his splendid book of 1873: "Hence  $J\pi$  represents the electromotive contact force at the junction acting in the positive direction. . . . Hence the assumption that the potential of a metal is to be measured by that of the air in contact with it must be erroneous, and the greater part of Volta's electromotive force must be sought for, not at the junction of the two metals, but at one or both of the surfaces which separate the metals from the air or other medium which forms the third element of the circuit."—'Treatise on Electricity and Magnetism,' vol. i. § 249.

of teachers and students. We find over and over again the statement that thermoelectric electromotive force is very much smaller than the Volta-contact electromotive force of dry metals. The truth is, Volta-electromotive force is found between metals all of one temperature, and is reckoned in volts, or fractions of a volt, without reference to temperature. If it varies with temperature, its *variations* may be stated in fractions of a volt per degree. On the other hand, thermoelectric electromotive force depends essentially on difference of temperature, and is essentially to be reckoned *per degree*; as for example, in fraction of a volt per degree.

§ 25. Volta's second fundamental discovery, that is, his discovery (§ 5 above) that vitreous and resinous electricity flow away from zinc and copper to insulated metals connected with them (for example, the two electrodes of an insulated electrometer) when the two metals are separated after having been in metallic contact, makes it quite certain that there must be electric force in the air or ether in the neighbourhood of two opposed surfaces of different metals metallically connected. This conclusion I verified about thirty-six years ago by experiments described in a letter to Joule, of January 21, 1862, which he communicated to the Literary and Philosophical Society of Manchester, published in the Proceedings of the Society and in 'Electrostatics and Magnetism' (§ 400) under the title of "A New Proof of Contact-electricity."

§ 26. Volta's second fundamental discovery also makes it certain that movable pieces of two metals, metallically connected, attract one another, except in the particular case when their free surfaces are Volta-electrically neutral to one another. This force, properly viewed, is a resultant of chemical affinity between thin surface layers of the two metals. And the work done by it, when they are allowed to approach through any distance towards contact between any parts of the surfaces, is the dynamical equivalent of the portion of their heat of combination due to the approach towards complete chemical combination constituted by the diminution of distance between the two bodies. To fix the ideas, let the metals be two plane parallel plates of zinc and copper, with distance between them small in comparison with their diameters, and let us calculate the amount of the attractive force between them at any distance. Let  $V$  be the difference of potentials of the air or ether very near the two metallic frontiers, but at distances from these frontiers amounting at least to several times the distance from molecule to nearest molecule in either metal (see footnote on § 16 above). The electric force in air or ether between these surfaces will be  $V/D$ , if  $D$  denotes the distance between them. Hence (our molecular microscopic binocular set aside) if  $\rho$  is the electric density of either of the opposed surfaces,  $A$  the area of either of the two, and  $P$  the attraction between them, we have

$$\frac{V}{D} = 4 \pi \rho, \quad P = \frac{1}{2} \rho \frac{V}{D} A.$$

Hence,

$$P = \frac{V^2 A}{8 \pi D^2}.$$

Hence the work done by electric attraction in letting them come from any greater distance asunder  $D'$  to any smaller distance  $D$  is:—

$$\frac{V^2 A}{8 \pi} \left( \frac{1}{D} - \frac{1}{D'} \right), \text{ or approximately, } \frac{V^2 A}{8 \pi D},$$

if  $D$  is very small in comparison with  $D'$ .

§ 27. For clean sand-papered copper and zinc\* we may take  $V$  as  $\frac{1}{2}$  of a volt c.g.s. electromagnetic, or  $\frac{1}{400}$  c.g.s. electrostatic.

Let now  $A$  be 1 sq. cm. and  $D$ ,  $\cdot 001$  of a centimetre. We find  $P$  equal to  $\cdot 249$  dyne, and the work done by attraction to this distance from any much greater distance is  $\cdot 000249$ . This is sufficient to heat  $5 \cdot 9 \times 10^{-12}$  grammes of water,  $1^\circ$ .

The table on the next page shows corresponding calculated results for various distances ranging from  $1/100$  of a centimetre to  $1/10^{10}$  of a centimetre.

Columns 5 and 6 are introduced to illustrate the relation between the electric attraction we are considering and chemical affinity as manifested by heat of combination. The "brass" referred to is an alloy of equal parts of zinc and copper, assumed to be of specific gravity 8 and specific heat  $\cdot 098$ .

§ 28. It would be exceedingly difficult, if indeed possible at all, to show by direct experiment, at any distance whatever, the force of attraction between the discs; as we see from the table at a distance of  $1/100$  of a centimetre it amounts to only  $1/400$  of a milligramme-heaviness; and to only  $2\frac{1}{2}$  grammes-heaviness at the distance  $10^{-5}$  of a centimetre, which is about  $\frac{1}{4}$  of the wave-length of ordinary yellow light. At the distances  $10^{-7}$ ,  $10^{-8}$ ,  $10^{-9}$  of a centimetre the calculated forces of attraction are 25 kilogrammes,  $2\frac{1}{2}$  tons,† and 250 tons. This last force is 2 or 8 times the breaking weight per square centimetre of the strongest steel (pianoforte wire), 6 times that of copper, 15 times that of zinc. We are, therefore, quite sure that the increase of attraction according to the inverse square of the distance is not continued to such small distances as  $10^{-9}$  of a centimetre; and at distances less than this, the electric attraction merges into molecular force between the two metals.

\* Peltier's measured values range from  $\cdot 68$  to  $\cdot 92$ , according to the physical condition left by less or more violent scrubbing with emery paper. The mean of these numbers is  $\cdot 77$ . Murray's range was still wider, from  $\cdot 68$  volt to  $1 \cdot 18$ , the smallest being for copper burnished, opposed to zinc scratched and polished with glass paper; and the largest, copper polished merely with emery paper, opposed to zinc polished and burnished.

† The metrical ton is about 2 per cent. less than ( $\cdot 984$  of) the British ton in general use through the British empire for a good many years before 1890, but destined, let us hope, to be rarely if ever used after the 19th century, when the French metrical system becomes generally adopted through the whole world.

METALLICALLY CONNECTED PARALLEL DISCS OF ZINC AND COPPER, EACH OF 1 SQUARE CENTIMETRE AREA, ATTRACTING ONE ANOTHER.

1	2	3	4	5	6
Distance between plates.	Force of attraction in dynes.*	Work in ergs.*	Equivalent of W in heat-units (gramme-water-1° Cent.).	Heat-units per gramme of brass disc of thickness D and area 1 sq. cm.	Rise of temperature produced by giving H to copper and zinc discs of thickness $\frac{1}{2}$ D, or to brass disc of thickness D and area 1 sq. cm. if specific heat constant at .093.
D.	P.	W.	H.	H + 8 D.	H + (8 X D X .093).
$10^{-2}$ of centimetre	$10^{-4} \times 25$ of dyne	$10^{-4} \times .25$ of erg	$10^{-12} \times .59$ of heat-unit		
$10^{-3}$ "	$10^{-2} \times 25$ "	$10^{-2} \times .25$ "	$10^{-11} \times .59$ "		
$10^{-4}$ "	25 dynes	$10^{-2} \times .25$ "	$10^{-10} \times .59$ "		
$10^{-5}$ "	$10^2 \times 25$ "	$10^{-1} \times .25$ "	$10^{-9} \times .59$ "		
$10^{-6}$ "	$10^4 \times 25$ "	.25 "	$10^{-8} \times .59$ "	.00074	.0079°
$10^{-7}$ "	$10^6 \times 25$ "	$10 \times .25$ ergs	$10^{-7} \times .59$ "	.074	.79°
$10^{-8}$ "	$10^8 \times 25$ "	$10^2 \times .25$ "	$10^{-6} \times .59$ "	.74	79°
$10^{-9}$ "	$10^{10} \times 25$ "	$10^3 \times .25$ "	$10^{-5} \times .59$ "	740	7,900°
$10^{-10}$ "	$10^{12} \times 25$ "	$10^4 \times .25$ "	$10^{-4} \times .59$ "	74,000	790,000°

\*The dyne is .981 of a milligramme heaviness in the latitude of Greenwich. For approximate estimate it may be taken as 2 per cent. less than 1 milligramme heaviness in any latitude. The erg is the work done by a force of 1 dyne acting through the space of 1 centimetre.

§ 29. Consider, now, a large number of discs of zinc and copper, each of 1 square centimetre area, and thickness  $D$ , and polished on both sides. On one side of each disc attach three very small columns, of length  $D$ , of glass or other insulating material, and place one disc on top of the insulators of another, zinc and copper alternately, so as to make a dry insulated pile of the metal discs, separated by air spaces each equal to the thickness  $D$ . If in the building of this pile each disc is kept metallically connected with the one over which it is placed, while it is being brought into its position, work will be done upon it by electric attraction to the amount shown in column 3, and the total work of electric attraction during the building of the pile will be the amount shown in column 3, multiplied by one less than the number of discs.

But if each disc, after being metallically connected with the one on which it is to be placed, till it comes within some considerable distance—say  $300 D$ , for example, from the disc over which it is to rest—is then disconnected and kept insulated while carried to its position in the pile, no work will be done on it by electric attraction. And if now, lastly, metallic connection is made between all the discs of the pile, currents pass from each copper to each zinc disc, and heat is generated to an amount equal to that shown in column 4, multiplied by one less than the number of discs; and if this heat is allowed to become uniformly diffused through the metals, they rise in temperature to the extent shown in column 6.

All these statements assume that the electric attraction increases according to the inverse square of the distance between opposed faces of zinc and copper. We have already (§ 28) seen that this assumption cannot be extended to such small distances as  $10^{-9}$  of a centimetre. We have now further proof of this conclusion beyond the possibility of doubt, because the large numbers in columns 5 and 6 for  $10^{-9}$  are enormously greater than any rational estimate we can conceive for the heat of combination of equal parts of zinc and copper per gramme of the brass formed. (See § 32 below.)

§ 30. When, on a Friday evening in February 1883—fourteen years ago—quoting from an article which had been published in *Nature* † in 1879, I first brought these views before the Royal Institution, we had no knowledge of the amount of heat of combination of zinc and copper, nor indeed of any other two metals. It appeared probable to us, from Volta's discovery of contact electricity between dry metals, that there must be some heat of combination; but I could then only express keenly-felt discontent with our ignorance of its amount. Now, however, after twenty-seven years' endurance, I am happily relieved since yesterday by Professor Roberts Austen, who most kindly undertook to help me in my preparations for this evening, with an investigation on the heat of combination of copper and zinc, by which he has found that the melting together of 30 per cent.

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\* 'Nature,' i. 551, "On the Size of Atoms."

of zinc with 70 per cent. of copper generates about 86 heat-units (gramme-water-Cent.) per gramme of the brass formed. I am sure you will all join with me in hearty thanks to him, both for this result and for his further great kindness in letting us now see a very beautiful experiment, demonstrating a large amount of heat of combination between aluminium and copper, in illustration of his mode of experimenting with zinc and copper, which could not be so conveniently put before you, because of the dense white fumes inevitable when zinc is melted in the open air.

[Experiment: A piece of solid aluminium dropped into melted copper: large rise of temperature proved by thermo-electric test. Result seen by all in large deflection of spot of light reflected from mirror of galvanometer.]

§ 81. Another method of investigating the heat of combination of metals, which I have long had in my mind, is to compare the heat evolved by the solution of an alloy in an acid with the sum of the heats of combination of its two constituents in mixed powders. The former quantity must be less than the latter by exactly the amount of the heat of combination. This investigation was undertaken a month ago by Mr. Galt, in the Physical Laboratory of the University of Glasgow, and he has already obtained promising results; but many experimental difficulties, as was to be expected, have presented themselves, and must be overcome before trustworthy results can be obtained.

[*Added Feb. 1898.*—By dissolving a gramme of a powdered alloy, and again a gramme of mixed powders of the two metals in the same proportion, in dilute nitric acid, Mr. Galt has now obtained approximate determinations of heats of combination for four different alloys, as shown in the following table:—

No.	Alloy.	Heat of combination per gramme of alloy in gramme-water- Cent. thermal units.
I.	.. { 48 per cent. zinc } .. { 52     "     copper } .. (Approximately chemical combining proportions.)*	77
II.	.. { 80 per cent. zinc } .. { 70     "     copper } ..	84·6
III.	.. { 76·7 per cent. silver } .. { 23·8     "     copper } .. (Approximately chemical combining proportions.)*	18
IV.	.. { 51·6 per cent. silver } .. { 48·4     "     copper } ..	7

\* The combining proportions are—

(i) 50·8 zinc with 40·2 copper,  
and (ii) 77·4 silver     "     22·6     "



The composition stated for the alloy in each case is the result of chemical analysis. No. I. was intended to be equal parts of zinc and copper (as being approximately the chemically combining proportions); but the alloy, which resulted from melting together equal parts, was found to have 4 per cent. more copper than zinc, there having no doubt been considerable loss of the melted zinc by evaporation. No. III. turned out on analysis to be, as intended, very nearly in the chemically combining proportions of silver and copper. No. IV. was intended to be equal parts of silver and copper, but analysis showed the deviation from equality stated in the table. The proportions of No. II. were chosen for the sake of comparison with Professor Roberts Austen's result (§ 30), and the agreement (34.6 and 36) is much closer than could have been expected, considering the great difference of the two methods and the great difficulties in the way of obtaining exact results which each method presents.

From a chemical point of view it is interesting to see, from Mr. Galt's results, how much more, both in the case of copper and zinc, and copper and silver, the heat of combination is, when the proportions are approximately the chemically combining proportions, than when they differ from these proportions to the extents found in Alloys II. and IV. Mr. Galt intends, in continuance of his investigation, to determine as accurately as he can the heats of combination of many different alloys of zinc and copper and of silver and copper, and so to find whether or not it is greatest when the proportions are exactly the chemically "combining proportions." He hopes also to make similar experiments with bismuth and antimony, using *aqua regia* as solvent.]

[§ 32. *February* 1898.—Looking now to column 5 of the table of § 27, we see from Professor Roberts Austen's result, 36 thermal units, for the heat of combination of 30 per cent. copper with 70 per cent. zinc, and from Galt's 77 thermal units for equal parts of copper and zinc, that the law of electric action on which the calculations of the tables are founded is utterly disproved for discs of metal of one one-thousand-millionth of a centimetre thickness, with air or ether spaces between them of the same thickness, but is not disproved for thicknesses of one one-hundred millionth of a centimetre.

Consider now our ideal insulated pile (§ 29) of discs  $10^{-3}$  of a centimetre thick, with air or ether spaces of the same thickness between them. Suddenly establish metallic connection between all the discs. The consequent electric currents will generate 7.4 thermal units, and heat the discs by  $79^{\circ}$  C. Take again the insulated column with thicknesses and distances of  $10^{-3}$  of a centimetre; remove the ideal glass separators and diminish the distance to  $10^{-9}$  of a centimetre (the thicknesses of discs being still  $10^{-3}$  of a centimetre). Now, with these smaller distances between two opposed areas, make metallic contact throughout the column by bending the corners (the discs for convenience being now supposed square); 74 thermal units will be

immediately generated, and the discs will rise  $790^{\circ}$  in temperature, and we have a column of hot brass—perhaps solid, perhaps liquid. This last statement assumes that the law of electric action, on which the table is founded, holds for discs  $10^{-8}$  of a centimetre thick, with ether or air spaces between them of  $10^{-9}$  of a centimetre. In reality it is probable that the law of electric action for discs  $10^{-8}$  of a centimetre thick, begins to merge into more complicated results of intermolecular forces, before the distance is as small as  $10^{-8}$  of a centimetre.

Resuming our mental molecular microscopic binocular (§ 16, footnote), we cannot avoid seeing molecular structures beginning to be perceptible at distances of the hundred-millionth of a centimetre, and we may consider it as highly probable that the distance from any point in a molecule of copper or zinc to the nearest corresponding point of another molecule is less than one one-hundred-millionth, and greater than one one-thousand-millionth of a centimetre.]

§ 33. In all that precedes I have, by frequent repetition of the phrase "air or ether," carefully kept in view the truth that the *dry* Volta contact-electricity of metals is, in the main, independent of the character of the insulating medium occupying space around and between the metals concerned in each experiment, and depends essentially on the chemical and physical conditions of molecules of matter in the thin surface stratum between the interior homogeneous metal and the external space, occupied by ether and dry or moist atmospheric air or any gas or vapour which does not violently attack the metal: or by ether with vapours only of mercury and glass and platinum and steel and vaseline (caulking the glass-stopcocks), as in Bottomley's experiments (§ 14 above).

This truth has always seemed to me convincingly demonstrated by Volta's own experiments, and I have never felt that that conviction needed further foundation; though of course I have not considered quite needless or uninformative, Pfaff's and my own and Pellat's repetitions and verifications, in different gases at different pressures, and Bottomley's extension of the demonstration to vacuum of  $2\frac{1}{2}$  millionths of an atmosphere. I am now much interested to see by Professor Oliver Lodge's report, already referred to (§ 4 above), that in the Bakerian Lecture to the Royal Society in 1806,\* Sir Humphry Davy, who had had contemporaneous knowledge of Volta's first and second discoveries, expressed himself thus clearly as to the validity of the second: "Before the experiments of M. Volta on the electricity excited by mere contact of metals were published, I had to a certain extent adopted this opinion," an opinion of Fabroni's; "but the new fact immediately proved that another power must necessarily be concerned, for it was not possible to refer the electricity exhibited by the opposition of metallic surfaces to any chemical alterations, particularly as the effect is more distinct in a dry atmo-

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\* Phil. Trans. 1807.

sphere, in which even the most oxidisable metals do not change, than in a moist one, in which many metals undergo oxidation."

§ 34. It is curious to find, thirty or forty years later, De la Rive explaining away Volta's second discovery by moisture in the atmosphere! Fifty-one years ago, when I first learned Volta's second discovery, by buying, in Paris, apparatus by which it has ever since been shown in the ordinary lectures of my class in the University of Glasgow, I was warned that De la Rive had found it wrong, and had proved it to be due to oxidation of the zinc by moisture from the air. I soon tested the value of this warning by the experiments of § 5 above, and a considerable variety of equivalent experiments, in one of which (real or ideal, I cannot remember which), a varnished zinc disc, scratched in places and moistened, sometimes on the scratched parts and sometimes where the varnish was complete, was tested in the usual manner by separating from contact with an unvarnished or varnished copper disc, with or without metallic connection when the discs were at their nearest.

[§§ 35-40 are added in Feb. 1898.]

§ 35. Within the last eighteen or twenty years there has been a tendency among some writers to fall back upon De la Rive's old hypothesis, of which there are signs in expressions quoted by Professor Oliver Lodge in his great and valuable report of 1884, and in some statements also of Professor Lodge's own views.

In what is virtually a continuation of this report in the 'Philosophical Magazine' a year later,\* we find the following with reference to writings of Helmholtz and myself on the contact-electricity of metals: "Both these contact theories, in explaining the Volta effect, ignore the existence of the oxidising medium surrounding the metals. My view explains the whole effect as the result of this oxygen bath, and of the chemical strain by it set up." With views seemingly unchanged, he returned to the subject at the end of 1897 with the following statement in the printed syllabus of his 'Six Lectures adapted to a Juvenile Auditory, on the Principles of the Electric Telegraph' (Royal Institution, Dec. 28, 1897, Jan. 8, 1898).

"Chemical method of producing a current—Voltaic cell—Two differently oxidisable metals immersed in an oxidising liquid and connected by a wire can maintain an electric current, through the liquid and through the wire, so long as the circuit is closed. [The same two metals immersed in a potentially oxidising gas and connected by a wire, can maintain an electric force or voltaic difference of potential in the space between them.]

"N.B.—No one need try too hard to understand sentences in brackets"

And lastly, after some correspondence which passed between us

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† Prof. O. Lodge 'On the Seat of the Electromotive Force in a Voltaic Cell,' Phil. Mag. Oct. 1885, p. 383.

in December, I have to-day (Feb. 14), received from him a "slightly amplified statement made in order to concentrate the differences," which he kindly gives me for publication as a supplement to the shorter statement from the syllabus.

*Amplification, February, 1898.*

"There is a true contact-force at a zinc-copper junction,\* which "on a simple and natural hypothesis (equivalent to taking an integration-constant as zero) can be measured thermoelectrically † and "is about  $\frac{1}{2}$  millivolt at  $10^{\circ}$  C.

"A voltaic force, more than a thousand times larger, † exists at "the junction of the metals with the medium surrounding them; and "in an ordinary case is calculable as the difference of oxidation-energies of zinc and copper; but it has nothing to do with the heat "of formation of brass.

*References:*

"Phil. Mag. [5].

"vol. xix. pp. 360 and 363, brass and atoms, pp. 487 and 494, summary.

"vol. xxi. pp. 270 and 275, thermoelectric argument.

"vol. xxii. p. 71, Ostwald experiment.

"August 1878, Brown experiment."

§ 36. With respect to the first of the two paragraphs of this last statement and the first two lines of the second, the wrongness of the view there set forth is pointed out in § 24 above. With respect to the last clause of the second paragraph and the statement quoted from the syllabus, I would ask any reader to answer these questions:—

(i.) What would be the efficacy of the supposed oxygen bath in the experiments of § 2 above with varnished plates of zinc and copper? or in Erskine Murray's experiment, described in his paper communicated last August to the Royal Society, in which metallic surfaces, scraped under melted paraffin so as to remove condensed oxygen or nitrogen from them, and leave fresh metallic surfaces in contact with a hydro-carbon, are subjected to the Voltaic experiment? or in Pfaff's and my own and Pellat's experiments with different gases, at ordinary and at low pressures, substituted for air? or in Bottomley's high vacuum and hydrogen and oxygen experiments (§ 14 above)?

(ii.) What would be the result of Volta's primary experiment, shown at the commencement of my lecture (§ 1 above), if it had been performed in some locality of the universe a thousand kilometres away from any place where there is oxygen? The insulators may be supposed to be made of rock-salt or solid paraffin, so that there may be no oxygen in any part of the apparatus. This I say because I understand that some anti-Voltaists have explained Bottomley's

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\* See footnote on § 16 above. K. Feb. 14, 1898.

† See § 24 above. K. Feb. 14, 1898.

experiments by the presence of vapour of silica from the glass, supplying the supposedly needful oxygen!

§ 37. The anti-Voltaists seem to have a superstitious veneration for oxygen. Oxygen is entitled to respect because it constitutes 50 per cent. of all the chemical elements in the earth's crust; but this gives it no title for credit as coefficient with zinc and copper in the dry Volta experiment, when there is none of it there. Oxygen has more affinity for zinc than for copper; so has chlorine and so has iodine. It is partially true that different metals—gold, silver, platinum, copper, iron, nickel, bismuth, antimony, tin, lead, zinc, aluminium, sodium—are for dry Volta contact electricity in the order of their affinities for oxygen; but it is probably quite as nearly true that they are in the order of their affinities for sulphur, or for oxy-sulphur ( $\text{SO}_2$ ) or for phosphorus or for chlorine or for bromine. It may or may not be true that metals can be unambiguously arranged in order of their affinities for any of these named substances; it is certainly true that they cannot be *definitely and surely* arranged in respect to their dry Volta contact-electricity. Murray's burnishing, performed on a metal which has been treated with Pellat's washing with alcohol and subsequent scratching and polishing with emery, alters the Volta quality of its surface far more than enough to change it from below to above several metals polished only by emery; and, in fact, Pellat had discovered large differences due to molecular condition without chemical difference, before Murray extended this fundamental discovery by finding the effect of burnishing.

§ 38. Returning to Professor Lodge's supposed oxygen bath (§ 35); if it exists between the zinc and copper plates, it diminishes or annuls or reverses the phenomenon, to explain which he invokes its presence (see § 5 above).

§ 39. Many years ago I found that ice, or hot glass, pressed on opposite sides by polished zinc and copper, produced deviations from the metallic zero of the quadrants of an electrometer metallically connected with them in the same direction as if there had been water in place of the ice or hot glass. From this I inferred that ice and hot glass, both of which had been previously known to have notable electric conductivity, acted as electrolytic conductors.

Experiments made by Maclean and Goto in the Physical Laboratory of the University of Glasgow in 1890,\* proved that polished zinc and polished copper, with fumes passing up between them from the flame of a spirit-lamp 30 centimetres below, gave, when metallically connected to the quadrants of an electrometer, deviations from the metallic zero in the same direction, and of nearly the same amount, as if cold water had been in place of the flame. This proved that flame acted as an electrolytic conductor. They also found that hot air from a large red-hot soldering bolt, put in the place of the spirit lamp, had no such effect; nor had breathing upon the plates, nor the vapour

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\* Phil. Mag., Aug. 1890.

of hot water, any effect of the kind. In fact hot air, and either cloudy or clear steam, act as very excellent insulators; but there is some wonderful agency in fumes from a flame, remaining even in cooled fumes, in virtue of which the electric effect on zinc and copper is nearly the same as if continuous water, instead of fumes, were between the plates and in contact with both.\*

A similar conclusion in respect to air traversed by ultra-violet light was proved by Righi, † Hallwachs, ‡ Elster and Geitel, § Branly. ¶ The same was proved for ordinary atmospheric air, with Röntgen rays traversing it between plates of zinc and copper, by Mr. Erskine Murray, in an experiment suggested by Professor J. J. Thomson, and carried out in the Cavendish Laboratory of the University of Cambridge.¶¶

§ 40. The substitution for ordinary air between zinc and copper, of ice or hot glass, or of air or gas modified by flame or by ultra-violet rays, or by Röntgen rays, or by uranium (§§ 41, 42 below), gives us, no doubt, what would to some degree fulfil Professor Lodge's idea of a "potentially-oxidising" gas, and each one of the six fails wholly or partially to "maintain electric force or voltaic difference of potential in the space between them." In fact, Professor Lodge's bracketed sentence, so far as it can be understood, would be nearer the truth if in it "cannot" were substituted for "can." I hope no reader will consider this sentence too short or sharp. I am quite sure that Professor Lodge will approve of its tone, because in his letter to me of the 14th, he says, "In case of divergence of view it is best to have both aspects stated as crisply and distinctly as possible, so as to emphasise the difference." I wish I could also feel sure that he will agree with it, but I am afraid I cannot, because in the same letter he says, "I am still unrepentant."

*Continuation of Lecture of May 21, 1897.*

§ 41. In conclusion, I bring before you one of the most wonderful discoveries of the century now approaching its conclusion, made by the third of three great men, Antoine Becquerel, Edmond Becquerel, Henri Becquerel—father, son and grandson—who by their inventive genius and persevering labour have worthily contributed to the total of the scientific work of their time; a total which has rendered the nineteenth century more memorable than any one of all the twenty-three centuries of scientific history which preceded it, excepting the seventeenth century of the Christian era.

You see this little box which I hold in my right hand, just as I received it three months ago from my friend Professor Moissan, who will be here this day week to show you his isolation of fluorine. It

\* Kelvin and Maclean, R.S.E. 1897.

† Wiedemann's Annalen, 34, 1888.

‡ Comptes Rendus, 1888, 1890.

† Rend. R. Acc. dei Lincei, 1888, 1889.

§ Ibid. 38, 41, 1888.

¶ Proc. R.S. March 1896.

induces electric conductivity in the air all round it. If I were to show you an experiment proving this, you might say it is witchcraft. But here is the witch. You see, when I open the box, a piece of uranium of about the size of a watch. This production of electric conductance in air is only one of many marvels of the "uranium rays" discovered a year ago by Henri Becquerel, of no other of which can I now speak to you, except that the wood and paper of this box, and my hand, are to some degree transparent for them.

I now take the uranium out of its box and lay it on this horizontal copper plate, fixed to the insulated electrode of the electrometer. I fix a zinc plate, supported by a metal stem which is in metallic connection with the sheath of the electrometer, horizontally over the copper plate at a distance of about one centimetre from the top of the uranium. Look at the spot of light; it has already settled to very nearly the position which you remember it took when we had a water-arc between the copper and zinc plates, connected as now, copper to insulated quadrants and zinc to the sheath. I now lift the uranium, insulating it from the copper plate by three very small pieces of solid paraffin, so as to touch neither plate, or, again, to touch the zinc but not the copper. This change makes but little difference to the spot of light. I tilt the uranium now to touch the zinc above and the copper below; the spot of light comes to the metallic zero as nearly as you can see. I leave it to itself now, resting on its paraffin supports and not touching the zinc, and the spot of light goes back to where it was; showing about three-quarters of a volt positive.

§ 42. I now take this copper wire, which is metallically connected with the zinc plate and the sheath of the electrometer, and bring it to touch the under side of the copper shelf on which the uranium is supported by its paraffin insulators. Instantly the spot of light moves towards the metallic zero, and after a few vibrations settles there. I break the contact; instantly the spot of light begins to return to its previous position, where it settles again in less than half a minute. You see, therefore, that if I re-make and keep made the metallic contact between the zinc and copper plates, a current is continuously maintained through the connecting wire, by which heat is generated and radiated away, or carried away by the air; as long as the contact is kept made. What is the source of the energy thus produced? If we take away the uranium, and send cool fumes from a spirit-lamp, or shed Röntgen rays or ultra-violet light, between the zinc and copper, the results of breaking and making contact would be just what you see with uranium. So would they be—you have already, in fact, seen them (§ 5)—without either Röntgen rays or ultra-violet light, but with the copper and zinc a little closer together and with a drop of water between them: and so would they be with dry ice, or with hot glass, between and touched by the zinc and copper. In each of these six cases we have a source of energy; the well-known electro-chemical energy given by the oxidation of zinc in the last

mentioned three cases; and the energy drawn upon by the cooled fumes, or by the Röntgen rays or ultra-violet light, acting in some hitherto unexplained manner, in the three other cases. We may conjecture evaporations of metals; we have but little confidence in the probability of the idea. Or does it depend on metallic carbides mixed among the metallic uranium? I venture on no hypothesis. Mr. Becquerel has given irrefragable proof of the truth of his discovery of radiation from uranium of something which we must admit to be of the same species as light, and which may be compared with phosphorescence. When the energy drawn upon by this light is known, then, no doubt, the *quasi* electrolytic phenomena, induced by uranium in air,\* which you have seen, will be explained by the same dynamical and chemical principles as those of the previously known electrolytic action of cooled fumes from a spirit-lamp, and of air traversed by Röntgen rays or ultra-violet light.

#### APPENDIX.

##### *On a Method of Measuring Contact Electricity.†*

IN my reprint of papers on Electrostatics and Magnetism (§ 400, of original date, January 1862) I described briefly this method, in connection with a new physical principle, for exhibiting contact electricity by means of copper and zinc quadrants substituted for the uniform brass quadrants of my quadrant electrometer. In an extensive series of experiments which I made in the years 1859-61, I had used the same method, but with movable discs for the contact electricity, after the method of Volta, and my own quadrant electrometer substituted for the gold-leaf electroscope by which Volta himself obtained his electric indications.

I was on the point of transmitting to the Royal Society a paper which I had written describing these experiments, and which I still have in manuscript, when I found a paper by Hankel in Poggendorf's 'Annalen' for January, 1862, in which results altogether in accordance with my own were given, and I withheld my paper till I might be able not merely to describe a new method, but if possible, add something to the available information regarding the properties of

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\* Experiments made in the Physical Laboratory of the University of Glasgow [§ 88 of Kelvin, Beattie and Smolan, Proc. R.S.E.; also 'Nature,' March 11, 1897, and Phil. Mag. March 1898] show this electrolytic conductivity to be produced by uranium to nearly the same amount in common air oxygen and carbonic acid; and to about one-third of the same amount in hydrogen, at ordinary atmospheric pressure; but only to about  $\frac{1}{100}$  of this amount in each of these four gases at pressures of 2 or 3 millimetres. There seems every reason to believe that it would be non-existent in high vacuum, such as that reached by Bottomley in his Volta-contact experiments (§ 14 above).

† First published in the British Association, Swansea meeting, August 1890, and 'Nature,' April 4. 1881.



matter to be found in Hankel's paper. I have made many experiments from time to time since 1861 by the same method, but have obtained results merely confirmatory of what had been published by Pfaff in 1820 or 1821, showing the phenomena of contact electricity to be independent of the surrounding gas, and agreeing in the main with the numerical values of the contact differences of different metals which Hankel had published; and I have therefore hitherto published nothing except the slight statements regarding contact electricity which appear in my 'Electrostatics and Magnetism.' As interest has been recently revived in the subject of contact electricity, the following description of my method may possibly prove useful to experimenters. The same method has been used to very good effect, but with a Bohnenberger electroscope instead of my quadrant electrometer, in researches on contact electricity by Mr. H. Pellat, described in the 'Journal de Physique' for May 1880.

The apparatus used in these experiments was designed to secure the following conditions: To support, within a metallic sheath, two circular discs of metal about four inches in diameter in such a way that the opposing surfaces should be exactly parallel to each other and approximately horizontal, and that the distance between them might be varied at pleasure from a shortest distance of about one-fiftieth of an inch to about a quarter or half an inch. This part of the apparatus I have called a "Volta-condenser." The lower plate, which was the insulated one, was fixed on a glass stem rising from the centre of a cast-iron sole plate. The upper plate was suspended by a chain to the lower end of a brass rod sliding through a steadying socket in the upper part of the sheath. An adjustable screw on this stem prevents the upper plate from being let down to nearer than about one-fiftieth of an inch, or whatever shortest distance may be wanted in any particular case. A stout brass flange fixed to the lower end of this rod bears three screws, one of which *S* is shown in the drawing, by which the upper plate can be adjusted to parallelism to the lower plate. The other apparatus used consisted of a quadrant electrometer, and in my original experiments an ordinary Daniell's cell, in my later ones a gravity Daniell's cell of the form which I described in 'Proc. R.S.' 1871 (pp. 253-259), with a divider by which any integral number of per cents. from 0 to 100 of the electromotive force of the cell could be established between any two mutually insulated homogeneous metals in the apparatus.

*Connections.*—The insulated plate was connected by a brass wire passing through the case of the Volta-condenser to the electrode of the insulated pair of quadrants. The upper plate was connected to the metal sheath of the Volta-condenser, and to the metal case of the electrometer, one pair of quadrants of which were also connected to the case. One of the two terminals of the divider, connected to the poles of the cell, was connected to the case of the electrometer. To the third terminal (the bar carrying the slider) was attached one of the contact wires, which was a length of copper wire having soldered

to its outer end a short piece of platinum. The other contact surface was a similar short piece of platinum fixed to the insulated electrode of the electrometer. Hence it will be seen that metallic connection between the two plates was effected by putting the divider at zero and bringing into contact the two pieces of platinum wire.

*Order of Experiment.*—The sliding piece of the divider was put to zero, and contact made and broken, and the upper plate raised: then the deflection of the spot of light was observed. These operations were repeated with the sliding piece at different numbers on the divider scale, until one was found at which the make-break and separation caused no perceptible deflection. The number thus found on the divider scale was the percentage of the electromotive force of the Daniell cell, which was equal to the contact electric difference of the plates in the Volt-condenser.

[*Addendum*, November 23, 1880.—Since the communication of this paper to the British Association, I have found that a dry platinum disc, kept for some time in dry hydrogen gas, and then put into its position in dry atmospheric air in the apparatus for contact electricity, becomes positive to another platinum disc which had not been so treated, but had simply been left undisturbed in the apparatus. The positive quality thus produced by the hydrogen diminishes gradually, and becomes insensible after two or three days.]

P.S.—On December 24, 1880, one of two platinum plates in the Volta-condenser was taken out; placed in dried oxygen gas for forty-five minutes; taken out, carried by hand, and replaced in the Volta-condenser at 12.30 on that day. It was then found to be negative to the platinum plate, which had been left undisturbed. The amount of the difference was about  $\cdot 33$  of a volt. The plates were left undisturbed for seventeen minutes in the condenser, and were then tested again, and the difference was found to have fallen to  $\cdot 29$  of a volt. At noon on the 25th they were again tested, and the difference found to be  $\cdot 18$ . The differences had been tested from time to time since that day, the plates having been left in the condenser undisturbed in the intervals. The following table shows the whole series of these results:—

Time.	Electric difference between surfaces of a platinum plate in natural condition, and a platinum plate after 45 minutes' exposure to dry oxygen gas.						
Dec. 24, 12.30 p.m.	..	..	..	..	..	..	$\cdot 33$ of a volt.
24, 12.47 p.m.	..	..	..	..	..	..	$\cdot 29$ "
25, noon	..	..	..	..	..	..	$\cdot 18$ "
27, noon	..	..	..	..	..	..	$\cdot 116$ "
28, 11.20 a.m.	..	..	..	..	..	..	$\cdot 097$ "
31, noon	..	..	..	..	..	..	$\cdot 047$ "
Jan. 4, 11.0 a.m.	..	..	..	..	..	..	$\cdot 042$ "
11, 11.40 a.m.	..	..	..	..	..	..	$\cdot 020$ "

Mr. Rennie, by whom these experiments were made during the recent Christmas holidays, had previously experimented on a platinum

plate which had been made the positive pole in an electrolytic cell with an electromotive force of one volt, tending to decompose water acidulated with sulphuric acid; the other pole being a piece of platinum wire. After the plate had been one hour under this influence in the electrolytic cell he removed it, and dried it by lightly rubbing it with a piece of linen cloth. He then placed it in the Volta-condenser, and found it to be negative to a platinum plate in ordinary condition; the difference observed was  $\cdot 27$  of a volt. This experiment was made on October 21; and on November 8 it was found that the difference had fallen from  $\cdot 27$  to  $\cdot 07$ . Mr. Rennie also made similar experiments with the platinum disc made the negative pole in an electrolytic cell, and found that this rendered the platinum positive to undisturbed platinum to a degree equal to about  $\cdot 04$  of a volt. The effect of soaking the platinum plate in dry hydrogen gas, alluded to in my first postscript, which also was observed by Mr. Rennie, was found to be about  $\cdot 11$  of a volt. Thus in the case of polarisation by hydrogen, as well as in the case of polarisation by oxygen, the effect of exposure to the dry gas was considerably greater than the effect of electro-plating the platinum with the gas by the electromotive force of one volt.

[K.]

Friday May 28, 1897.

LUDWIG MOND, Esq. Ph.D. F.R.S. Vice-President,  
in the Chair.

PROFESSEUR HENRI MOISSAN, Membre de l'Académie des Sciences,  
Paris.

*Le Fluor.*

MILORDS, Mesdames et Messieurs,—J'ai été heureux de répondre à votre appel, et je tiens tout d'abord à vous remercier de l'honneur que vous avez bien voulu me faire en me demandant cette conférence.

On connaissait depuis longtemps un minéral curieux auquel on a donné le nom de fluorine et que l'on rencontre dans la nature en gros cristaux cubiques, incolores ou teintés de vert ou de violet. Cette fluorine est un composé binaire formé d'un métal, le calcium uni à un autre corps simple qu'il avait été impossible d'isoler jusqu'ici et auquel on a donné le nom de fluor.

Ce fluorure de calcium a été comparé bien souvent au chlorure de sodium dont les chimistes connaissent parfaitement la composition. En effet, entre les fluorures et les chlorures, il y a de grandes et profondes analogies : le chlorure et le fluorure de potassium cristallisent tous deux dans le système cubique. Les propriétés principales des chlorures sont semblables à celles des fluorures. Ils fournissent le plus souvent des réactions parallèles ; traités par l'acide sulfurique ils produisent les uns et les autres des acides hydrogénés solubles dans l'eau et donnant à l'air d'abondantes fumées.

Outre le fluorure de calcium, on trouve encore, dans la nature, d'autres composés renfermant du fluor. On connaît, par exemple, une combinaison complexe de phosphate de chaux et de fluorure de calcium à laquelle on a donné le nom d'apatite.

Ce minéral, qui se présente parfois en très jolis cristaux, a pu être obtenu synthétiquement dans les laboratoires, mais ce qui est plus important, Henri Sainte-Claire Deville a pu préparer une apatite chlorée, et ce nouveau composé se présente en cristaux identiques à ceux de l'apatite fluorée. On est donc en droit de dire que, dans ces combinaisons le chlore peut remplacer le fluor, s'y substituer. C'est là une analogie remarquable, un lien qui réunissait le chlore, bien étudié, bien connu, à ce corps simple, non encore isolé, le fluor.

Ai-je besoin de vous citer d'autres exemples ? Ils ne nous man-

queront pas. On connaît la wagnérite, fluorée naturelle; on peut préparer le composé similaire chloré.

Ces analogies du chlore et du fluor se poursuivent plus loin.

Traisons du sel marin, du chlorure de sodium, par de l'acide sulfurique. Vous voyez qu'il se produit aussitôt un abondant dégagement d'acide chlorhydrique gazeux.

Faisons de même pour le fluorure de sodium. Ajoutons dans un vase de plomb de l'acide sulfurique à un fluorure alcalin. Nous verrons des fumées intenses se produire. Dans l'un et l'autre cas, nous aurons dégagé un corps gazeux à une température de  $+20^{\circ}$  (centigrade), fumant abondamment à l'air, incolore, possédant les caractères d'un acide énergétique, s'unissant à l'état anhydre avec l'ammoniaque, très soluble dans l'eau et s'y combinant avec une grande élévation de température.

Si nous donnons au fluorure de sodium, au composé binaire du fluor et du sodium, la formule  $\text{NaF}$ , celle du corps acide produit par l'action de l'acide sulfurique ne peut être que  $\text{HF}$ . Les deux réactions sont identiques.

Le corps gazeux, acide, produit dans cette réaction, est donc une combinaison de fluor et d'hydrogène, un corps analogue à l'acide chlorhydrique auquel nous donnerons le nom d'acide fluorhydrique.

Mais, dans les sciences naturelles l'analogie ne suffit pas; la méthode scientifique ne peut admettre que ce qui est rigoureusement démontré. Il fallait donc tout d'abord prouver que l'acide fluorhydrique était un acide hydrogéné. Et ceci, messieurs, va nous reporter au commencement de ce siècle. Vous savez combien fut grande l'influence de Lavoisier sur l'essor de la chimie en tant que science véritable. Vous savez combien ce grand esprit, par l'emploi continu de la balance dans les réactions, fournit à la science que nous étudions une rigueur mathématique. Frappé du rôle important de l'oxygène dans la combustion, il crut que cet élément était indispensable à la formation des acides. Pour Lavoisier, tout acide était un corps oxygéné; l'acide chlorhydrique fut donc, d'après les théories de Lavoisier, considéré comme renfermant de l'oxygène, et il en fut de même, par analogie, pour l'acide fluorhydrique.

C'est à votre grand savant Humphry Davy que revient l'honneur d'avoir démontré que l'acide fluorhydrique ne renfermait pas d'oxygène. Mais permettez-moi, avant d'arriver aux belles recherches de Davy, de vous rappeler l'historique de la découverte de l'acide fluorhydrique. Nous ne nous arrêterons pas aux recherches de Margraff sur ce sujet, publiées en 1768, mais nous n'oublierons pas que ce fut Scheele qui caractérisa l'acide fluorhydrique en 1771, sans arriver toutefois à l'obtenir à l'état de pureté. En 1809, Gay-Lussac et Thénard reprirent l'étude de cette préparation et arrivèrent à produire un acide assez pur, très concentré, mais qui était loin d'être anhydre. L'action de l'acide fluorhydrique sur la silice et les silicates fut alors parfaitement élucidée.

Reportons-nous maintenant vers l'année 1818, époque où Davy

reprënd l'étude de l'acide fluorhydrique. Peu de temps auparavant, Ampère, dans deux lettres adressées à Humphry Davy, avait émis cette opinion que l'acide fluorhydrique pouvait être considéré comme formé par la combinaison de l'hydrogène avec un corps simple encore inconnu, le fluor, en un mot que c'était un acide non oxygéné.

Davy, qui partageait cette idée, chercha donc tout d'abord à démontrer que l'acide fluorhydrique ne renferme pas d'oxygène. Pour cela, il neutralise l'acide fluorhydrique par de l'ammoniaque et, en chauffant fortement ce sel dans un appareil en platine, il ne recueille dans la partie froide que le fluorhydrate d'ammoniaque sublimé sans aucune trace d'eau.

Répétons la même expérience, mais avec un acide oxygéné; prenons de l'acide sulfurique que nous neutraliserons par de l'ammoniaque; nous obtenons ainsi du sulfate d'ammoniaque. Si nous chauffons alors ce sel dans le même appareil en platine, il fond vers 140°, puis vers 180° il se décompose en ammoniaque et en bisulfate, enfin ce dernier sel se transforme par une nouvelle élévation de température en bisulfite d'ammoniaque volatil, en azote et en eau.

Ainsi, en chauffant fortement le sulfate d'ammoniaque, il y a eu formation d'eau. Et dans cette expérience de Davy, lorsque l'on se trouve en présence d'un acide oxygéné, la quantité d'eau recueillie est assez grande pour être admise d'une façon indiscutable. Le fluorhydrate d'ammoniaque, de même que le chlorhydrate, ne fournissant pas d'eau par sa décomposition, on était donc conduit à dire que l'acide fluorhydrique ne renfermait pas d'oxygène et qu'il était analogue à l'acide chlorhydrique. Or, on sait par démonstration expérimentale que l'acide chlorhydrique est formé de chlore et d'hydrogène; il est donc logique de penser que l'acide fluorhydrique est produit par la combinaison de l'hydrogène avec le fluor.

Cette expérience importante, faite par des mains exercées, ne parvint cependant pas à faire admettre d'une façon générale, l'existence des hydracides.

Les idées de Lavoisier sur le rôle de l'oxygène dans la formation des acides, idées qui avaient été combattues au début, étaient alors si bien admises que beaucoup d'esprits se refusaient à croire à l'existence d'acides hydrogénés. Ce ne fut qu'après les recherches mémorables de Gay-Lussac sur le cyanogène et sur l'acide cyanhydrique, qu'il fut démontré d'une façon indiscutable qu'il pouvait exister des acides énergiques ne renfermant pas trace d'oxygène.

D'ailleurs, quand nous avons à comparer les combinaisons acides formées par le chlore, par exemple, ou le soufre, avec l'hydrogène, nous avons là deux types de composés tout à fait différents.

Prenons un volume de chlore et un volume d'hydrogène; sous l'action de la lumière ou d'une étincelle d'induction, ils s'uniront pour former deux volumes de gaz acide chlorhydrique, composé ayant toutes les propriétés d'une acide très énergique.

Si nous combinons deux volumes d'hydrogène à un volume de vapeur de soufre, nous obtiendrons deux volumes de gaz hydrogène

sulfuré, possédant encore une réaction acide, il est vrai, mais incomparablement plus faible que celle de l'acide chlorhydrique.

Il est bien évident que, par ses réactions énergiques, par le dégagement de chaleur qu'il produit au contact de l'eau et des bases, l'acide fluorhydrique doit être comparé à l'acide chlorhydrique et non à l'acide sulfhydrique. Il se rapproche absolument de cet acide chlorhydrique formé d'un volume de chlore et d'un volume d'hydrogène unis sans condensation.

Permettez-moi maintenant de vous rappeler une expérience beaucoup plus récente de Gorre. Ce chimiste a chauffé du fluorure d'argent dans une atmosphère d'hydrogène. Il a vu, dans ces conditions, le volume gazeux doubler ; il semble donc bien que l'acide fluorhydrique soit formé d'un volume d'hydrogène uni à un volume de ce corps simple non encore isolé, le fluor. De plus, c'est bien ce même corps simple qui a quitté le fluorure d'argent pour s'unir à l'hydrogène et produire l'acide fluorhydrique dont nous venons de parler précédemment.

Ainsi, messieurs, sans préparer ce fluor, sans pouvoir le séparer des corps avec lesquels il est uni, la chimie était parvenue à étudier et à analyser un grand nombre de ses combinaisons. Le corps n'était pas isolé et cependant sa place était marquée dans nos classifications. Et c'est là ce qui nous démontre bien l'utilité d'une théorie scientifique : théorie qui sera regardée comme vraie pendant un certain temps, qui résumera les faits et permettra à l'esprit de nouvelles hypothèses, causes premières d'expériences, qui, peu à peu détruiront cette même théorie, pour la remplacer par une autre plus en harmonie avec les progrès de la science.

C'est ainsi que certaines propriétés du fluor étaient prévues avant même que son isolement ait été possible.

Voyons maintenant quels ont été les essais tentés, non seulement sur cet acide fluorhydrique, mais encore sur les fluorures, pour arriver à isoler le fluor.

Je vous parlais tout à l'heure des expériences de Davy, dans lesquelles il a démontré notamment que l'acide fluorhydrique ne renfermait pas d'oxygène. Outre ces expériences, Davy en a fait un grand nombre d'autres que je rappellerai en les résumant.

On peut d'une façon générale diviser les recherches entreprises sur le fluor en deux grandes classes :

1°. Expériences faites par voie électrolytique s'adressant soit à l'acide soit aux fluorures.

2°. Expériences faites par voie sèche. Dès le début de ces recherches, il était à prévoir que le fluor décomposerait l'eau quand on pourrait l'isoler ; par conséquent, toutes les tentatives qui ont été faites par la voie humide depuis les premiers travaux de Davy le furent sans aucune espèce de chance de succès.

Humphry Davy a fait beaucoup d'expériences électriques, et ces expériences il les a exécutées dans des appareils en platine ou en chlorure d'argent fondu et au moyen de la puissante pile de la Société royale.

Il a reconnu que l'acide fluorhydrique se décomposait tant qu'il contenait de l'eau et qu'ensuite le courant semblait passer avec beaucoup plus de difficulté. Il a essayé aussi de faire jaillir des étincelles dans l'acide concentré, et il a pu, dans quelques essais, obtenir par cette méthode une petite quantité de gaz. Mais l'acide, bien que refroidi, ne tardait pas à se réduire en vapeurs : le laboratoire devenait rapidement inhabitable. Davy fut même très malade pour s'être exposé à respirer les vapeurs d'acide fluorhydrique et il conseille aux chimistes de prendre de grandes précautions pour éviter l'action de cet acide sur la peau et sur les bronches. Vous savez, messieurs, que Gay-Lussac et Thénard avaient eu également beaucoup à souffrir de ces mêmes vapeurs acides.

Les autres expériences de Davy (je ne puis les citer toutes) ont été faites surtout en faisant réagir le chlore sur les fluorures. Elles présentaient des difficultés très grandes, car on ignorait à cette époque l'existence des fluorhydrates de fluorures et l'on ne savait point préparer la plupart des fluorures anhydres.

Ces recherches de Davy sont, comme on pouvait s'y attendre, de la plus haute importance, et une propriété remarquable du fluor a été mise en évidence par ce savant : dans les recherches où il avait été possible de produire une petite quantité de ce radical des fluorures, le platine ou l'or des vases dans lesquels se faisait la réaction était profondément attaqué. Il s'était formé dans ce cas des fluorures d'or ou de platine.

Davy a varié beaucoup les conditions de ces expériences. Il a répété l'action du chlore sur un fluorure métallique dans des vases de soufre, de charbon, d'or, de platine, etc. ; il n'est jamais arrivé à un résultat satisfaisant.

Il est conduit ainsi à penser que le fluor possédera sans doute une activité chimique beaucoup plus grande que celle des composés connus.

Et en terminant son mémoire Humphry Davy indique que ces expériences pourraient peut-être réussir si elles étaient exécutées dans des vases en fluorine. Nous allons voir que cette idée va être reprise par différents expérimentateurs. La lecture du travail de Davy vous intéresse, vous captive au plus haut point. Je ne puis mieux comparer ce beau mémoire qu'à ces tableaux de maître auxquels le temps ajoute un nouveau charme. On ne se lasse jamais de les admirer et l'on y découvre sans cesse de nouveaux détails et de nouvelles beautés.

C'est en opérant dans des appareils en fluorure de calcium que les frères Knox essayèrent de décomposer le fluorure d'argent par le chlore. La principale objection à faire à leurs expériences repose sur ce fait que le fluorure d'argent employé n'était pas sec. Il est en effet très difficile de déshydrater complètement les fluorures de mercure et d'argent. De plus, nous verrons, par les recherches de Fremy, que l'action du chlore sur les fluorures tend plutôt à former des produits d'addition, des fluochlorures, qu'à chasser le fluor et à le mettre en liberté.

En 1848, Louyet en opérant aussi dans des appareils en fluorine,



étudia une réaction analogue : il fit réagir le chlore sur le fluorure de mercure. Les objections que l'on peut faire aux recherches des frères Knox s'appliquent aussi aux travaux de Louyet. Fremy a démontré que le fluorure de mercure préparé par le procédé de Louyet renfermait encore une notable quantité d'eau. Aussi les résultats obtenus étaient assez variables. Le gaz recueilli était un mélange d'air, de chlore et d'acide fluorhydrique, dont les propriétés se modifiaient suivant la durée de la préparation.

Les frères Knox se plaignirent beaucoup de l'action de l'acide fluorhydrique sur les voies respiratoires, et, à la suite de leurs travaux l'un d'eux rapporte qu'il a passé trois années à Gênes, et en est revenu encore très souffrant. Quant à Louyet, entraîné par ses recherches, il ne prit pas assez de précautions pour éviter l'action irritante des vapeurs d'acide fluorhydrique, et il paya de sa vie son dévouement à la science.

Ces recherches de Louyet amenèrent Fremy à reprendre vers 1850 cette question de l'isolement du fluor. Fremy étudia d'abord avec méthode les fluorures métalliques ; il démontra l'existence de nombreux fluorhydrates de fluorures, indiqua leurs propriétés et leur composition. Puis, il fit réagir un grand nombre de corps gazeux sur ces différents fluorures ; l'action du chlore, de l'oxygène fut étudiée avec soin. Enfin, toute son attention fut attirée sur l'électrolyse des fluorures métalliques.

La plupart de ces expériences était faite dans des vases de platine à des températures parfois très élevées. Lorsque, après cette étude général des fluorures, Fremy reprit l'action du chlore sur les fluorures de plomb, d'antimoine, de mercure et d'argent, il montra nettement la presque impossibilité d'obtenir à cette époque ces fluorures absolument secs. Aussi l'on comprend que, dans ces recherches électrolytiques, ce savant se soit adressé surtout au fluorure de calcium.

Ayant vu combien les fluorures retiennent l'eau avec avidité, il revient toujours à cette fluorine, qu'on trouve parfois dans la nature dans un grand état de pureté, et absolument anhydre. C'est ce fluorure de calcium maintenu liquide, grâce à une haute température, qu'il va électrolyser dans un vase de platine.

Dans ces conditions, le métal calcium se porte au pôle négatif, et l'on voit, autour de la tige de platine qui constitue l'électrode négative et qui se ronge avec rapidité, un bouillonnement indiquant la mise en liberté d'un nouveau corps gazeux.

Certainement, dans ces expériences, du fluor a été mis en liberté, mais, messieurs, représentez-vous cette électrolyse faite à la température du rouge vif. Combien l'expérience devient difficile dans ces conditions ; comment recueillir le gaz ? comment en constater les propriétés ? Ce corps gazeux déplace l'iode des iodures ; mais, aussitôt que l'on tente quelques essais, le métal alcalin, mis en liberté, perce la paroi de platine ; tout est à recommencer, l'appareil est mis hors d'usage.

Loin de se décourager par les insuccès, Fremy apporte, au contraire, dans ces recherches, une persévérance incroyable. Il varie ses expériences, modifie ses appareils, et les difficultés ne font que l'encourager à poursuivre son étude.

Deux faits importants se dégagent tout d'abord de ses travaux : l'un qui est entré immédiatement dans le domaine de la science ; l'autre qui semble avoir frappé beaucoup moins les esprits.

Le premier c'est la préparation de l'acide fluorhydrique anhydre, de l'acide fluorhydrique pur. Jusqu'aux recherches de Fremy, on avait ignoré l'existence de l'acide fluorhydrique vraiment privé d'eau. Ayant préparé et analysé le fluorhydrate de fluorure de potassium, Fremy s'en sert aussitôt pour obtenir l'acide fluorhydrique pur et anhydre.

Il prépare ainsi un corps gazeux à la température ordinaire qui se condense dans un mélange réfrigérant en un liquide incolore très avide d'eau. Voilà donc une réaction d'une grande importance. préparation de l'acide fluorhydrique pur.

Je tiens à vous faire remarquer en passant que le jour où Humphry Davy a électrolysé l'acide fluorhydrique concentré, le liquide mauvais conducteur qu'il obtenait à la fin de son expérience était de l'acide fluorhydrique à peu près anhydre.

Le second fait, qui a passé je dirai presque inaperçu et qui m'a vivement intéressé, surtout à la fin de mes recherches, c'est que le fluor a la plus grande tendance à s'unir à presque tous les composés par voie d'addition.

En un mot, le fluor forme avec facilité des composés ternaires et quaternaires. Faisons réagir le chlore sur un fluorure ; au lieu d'isoler le fluor, nous préparerons un fluochlorure. Employons l'oxygène, nous ferons un oxyfluorure. Cette propriété nous explique l'insuccès des essais de Louyet, des frères Knox et d'autres opérateurs. Même en agissant sur les fluorures secs, dans une atmosphère de chlore, de brome ou d'iode, nous aurons plutôt des composés ternaires que du fluor libre. Ce fait a été nettement mis en évidence par Fremy. Et le mémoire de ce savant comportait un si grand nombre d'expériences, qu'il semble avoir découragé les chimistes, arrêté l'essor de nouvelles tentatives. Depuis 1856, date de la publication du mémoire de M. Fremy, les recherches sur l'acide fluorhydrique et sur l'isolement du fluor sont peu nombreuses. La question paraît subir un temps d'arrêt. Cependant, en 1869, M. Gorre reprend avec méthode l'étude de l'acide fluorhydrique. Il part de l'acide fluorhydrique anhydre préparé par la méthode de Fremy ; il détermine son point d'ébullition, sa tension de vapeur aux différentes températures, enfin ses principales propriétés. Son mémoire est d'une exactitude remarquable. Des nombreuses recherches de Gorre, nous ne retiendrons pour le moment que les suivantes, sur lesquelles je veux appeler votre attention.

Ce savant électrolyse dans un appareil spécial de l'acide fluorhydrique anhydre contenant une petite quantité de fluorure de platine,

de telle sorte qu'il puisse recueillir les gaz produits à chaque électrode ; il voit au pôle négatif se dégager de l'hydrogène en abondance, tandis que la tige qui terminait le pôle positif était rongée avec rapidité. Ce phénomène était identique à celui obtenu par Fremy dans l'électrolyse du fluorure de calcium. Gorre vérifie ensuite cette observation de Faraday, que l'acide fluorhydrique contenant de l'eau laisse passer le courant, mais que l'acide fluorhydrique absolument pur, bien anhydre, n'est nullement conducteur. Dans une de ses expériences, Gorre essaye d'électrolyser de l'acide fluorhydrique qui, par suite d'une impureté, était bon conducteur, et voulant éviter l'usure de l'électrode, il y substitue une baguette de charbon.

Ce charbon, il le prépare avec soin, en chauffant dans un courant d'hydrogène un bois dense, qui lui fournit une tige sonore, bonne conductrice de l'électricité. L'appareil étant monté, il commence l'expérience ; aussitôt une violente explosion se produit, les morceaux de charbon sont brisés et projetés aux extrémités du laboratoire. Gorre répète l'expérience plusieurs fois ; le résultat est toujours le même. Nous pouvons aujourd'hui donner l'explication de ce phénomène.

Le charbon qu'il préparait ainsi par distillation d'un bois très dur était rempli d'hydrogène. Vous savez tous, messieurs, combien les gaz se condensent avec facilité dans le charbon ; les belles expériences de Melsens l'ont établi d'une façon très nette. Lorsque l'on électrolyse ensuite de l'acide fluorhydrique conducteur, en plaçant au pôle positif un semblable charbon, il se dégageait du fluor qui s'unit à l'hydrogène, comme nous le verrons plus loin, en produisant une violente détonation. Dans cette expérience de Gorre une petite quantité de fluor avait été mise en liberté, et c'est à sa combinaison avec l'hydrogène occlus dans le charbon que l'explosion était due.

Et maintenant, messieurs, j'arrive aux expériences nouvelles dont j'ai à vous entretenir.

Je suis parti dans ces recherches d'une idée préconçue. Si l'on suppose pour un instant que le chlore n'ait pas encore été isolé, bien que nous sachions préparer les chlorures de phosphore et d'autres composés similaires, il est de toute évidence que l'on augmentera les chances que l'on peut avoir d'isoler cet élément en s'adressant aux composés que le chlore peut former avec les metalloïdes.

Il me semblait qu'on obtiendrait plutôt du chlore, en essayant de décomposer le pentachlorure de phosphore ou l'acide chlorhydrique qu'en s'adressant à l'électrolyse du chlorure de calcium ou d'un chlorure alcalin.

Ne doit-il pas en être de même pour le fluor ?

Enfin le fluor étant, d'après les recherches antérieures et particulièrement celles de Davy, un corps doué d'affinités très énergiques, on devait pour pouvoir recueillir cet élément, opérer à des températures aussi basses que possible.

Telles sont les idées générales qui nous ont amené à reprendre d'une façon systématique l'étude des combinaisons formées par le fluor et les metalloïdes.

Je me suis adressé tout d'abord au fluorure de silicium, et j'ai été frappé, dès ces premières recherches, de la grande stabilité de ce composé. Sauf les métaux alcalins, qui, au rouge sombre, le dédoublent avec facilité, peu de corps agissent sur le fluorure de silicium. Il est facile de se rendre compte de cette propriété si l'on remarque que sa formation est accompagnée d'un très grand dégagement de chaleur. M. Berthelot a démontré depuis longtemps que les corps composés sont d'autant plus stables qu'ils dégagent plus de chaleur au moment de leur production.

J'estimais donc, à tort ou à raison, avant même d'avoir isolé le fluor, que, si l'on parvenait jamais à préparer ce corps simple, il devait se combiner avec incandescence au silicium cristallisé. Et chaque fois que, dans ces longues recherches j'espérais avoir mis du fluor en liberté, je ne manquais pas d'essayer cette réaction; on verra plus loin qu'elle m'a parfaitement réussi.

Après ces premières expériences sur le fluorure de silicium, j'ai entrepris des recherches sur les composés du fluor et du phosphore.

M. Thorpe a découvert le composé  $\text{PhFl}^5$  un pentafluorure de phosphore; j'ai préparé le composé  $\text{PhFl}^3$  et j'ai porté toute mon attention sur les réactions qui permettaient d'essayer un dédoublement. J'ai fait cette expérience à laquelle avait songé Humphry Davy, de faire brûler le trifluorure de phosphore dans l'oxygène, et je me suis aperçu qu'il n'y avait pas eu formation d'acide phosphorique et mise en liberté du fluor, comme l'espérait le savant anglais, mais que le trifluorure et l'oxygène s'étaient unis pour donner un nouveau corps gazeux, l'oxyfluorure de phosphore.

N'était-ce pas là un nouvel exemple de cette facilité que possède le fluor de fournir des produits d'addition?

J'ai tenté alors, mais inutilement, l'action de l'étincelle d'induction sur le trifluorure de phosphore. Cependant le pentafluorure de phosphore découvert par M. Thorpe a pu être dédoublé par de très fortes étincelles en trifluorure de phosphore et fluor.

Cette expérience était faite dans une éprouvette de verre sur la cuve à mercure; vous pensez bien qu'immédiatement, il se produisait du fluorure de mercure et du fluorure de silicium. On ne pouvait pas espérer dans ces conditions conserver le fluor, même noyé dans un excès de pentafluorure. J'ai donc songé à une autre réaction.

On savait, depuis les recherches de Fremy, que le fluorure de platine, produit dans l'électrolyse des fluorures alcalins, se décomposait sous l'influence d'une température élevée. Ayant constaté que les fluorures de phosphore sont facilement absorbés à chaud par la mousse de platine, avec production finale de phosphure de platine, nous avons pensé que ce procédé de préparation du fluorure de platine permettrait d'isoler le fluor. En chauffant peu d'abord, l'absorption du fluorure de phosphore, par exemple, donnerait un mélange de phosphore et de fluorure de platine, et la quantité de ce dernier étant assez grande, une élévation de température pourrait en dégager le fluor. Ces expériences et d'autres analogues ont été tentées dans les

conditions les plus propres à en assurer le succès ; elles ont fourni des résultats intéressants, mais qui n'avaient pas une netteté suffisante pour résoudre la question de l'isolement du fluor.

En même temps que se poursuivaient les études précédentes, je préparais le trifluorure d'arsenic qui avait été obtenu par Dumas dans un grand état de pureté ; je déterminais ses constantes physiques ainsi que quelques propriétés nouvelles, et j'apportais tous mes soins à étudier l'action du courant électrique sur ce composé.

Le fluorure d'arsenic, corps liquide à la température ordinaire, composé binaire formé d'un corps solide, l'arsenic et d'un corps gazeux, le fluor, semblait se prêter dans d'excellentes conditions à des expériences d'électrolyse.

J'ai dû, à quatre reprises différents, interrompre ces recherches sur le fluorure d'arsenic, dont le maniement est plus dangereux que celui de l'acide fluorhydrique anhydre et dont les propriétés toxiques m'avaient mis dans l'impossibilité de continuer ces expériences.

Je suis arrivé cependant à électrolyser ce composé en employant le courant produit par 90 éléments Bunsen.

Dans ces conditions, le courant passe d'une façon continue ; l'arsenic se dépose à l'état pulvérulent au pôle négatif, et l'on voit se former sur l'électrode positive des bulles gazeuses qui montent dans le liquide mais sont absorbées presque aussitôt. Le fluor mis en liberté est repris de suite par le trifluorure d'arsenic  $\text{AsF}_3$  qui passe à l'état de pentafluorure  $\text{AsF}_5$ . Cette expérience, poursuivie pendant longtemps, ne m'a pas donné le fluor ; mais elle m'a fourni de précieux renseignements sur l'électrolyse des composés fluorés liquides, et elle m'a conduit à la décomposition de l'acide fluorhydrique anhydre.

Pour arriver à l'électrolyse de l'acide fluorhydrique, j'avais fait faire un petit appareil que vous avez sous les yeux et qui est formé d'un tube en U en platine portant sur chaque branche un tube abducteur placé au-dessus du niveau du liquide.

Les deux ouvertures de ce tube en U devaient être fermées par des bouchons de liège imbibés au préalable de paraffine ainsi que nous l'avions fait dans toutes nos expériences sur l'électrolyse du fluorure d'arsenic.

Un fil de platine traversait chaque bouchon et était mis en communication avec une pile de cinquante éléments Bunsen.

Nous avons préparé tout d'abord de l'acide fluorhydrique pur et anhydre, et nous avons vu que ce liquide, ainsi que l'avait indiqué Faraday et ensuite Gorre, ne conduisait nullement le courant.

L'expérience a été variée de bien des façons, le résultat est toujours le même. Avec le courant fourni par 90 éléments Bunsen, la décomposition ne se produit que lorsqu'on s'adresse à un acide hydraté, et cette décomposition s'arrête aussitôt que toute l'eau a été séparée en hydrogène et oxygène. Il semble donc impossible d'obtenir, par ce procédé, le dédoublement de l'acide fluorhydrique en ses éléments : hydrogène et fluor.

Je me suis souvenu à ce moment, que, dans les études précédentes

sur le fluorure d'arsenic, j'avais essayé de rendre ce liquide bon conducteur, en l'additionnant d'une petite quantité de fluorure de manganèse ou de fluorhydrate de fluorure de potassium. Ce procédé fut appliqué à l'acide fluorhydrique, et c'est alors qu'après trois années de recherches, j'arrivai à la première expérience importante sur l'isolement du fluor.

L'acide fluorhydrique contenant du fluorhydrate de fluorure de potassium se décompose sous l'action du courant et, dans l'appareil que vous avez sous les yeux, on peut obtenir au pôle négatif un dégagement régulier de gaz hydrogène. Qu'obtient-on au pôle positif ? Rien. Une légère augmentation de pression, voilà tout. Seulement, en démontant l'appareil, on remarque que le bouchon de liège du pôle positif a été brûlé, carbonisé, sur une profondeur d'un centimètre. Le bouchon de liège paraffiné du pôle négatif n'a pas été altéré. Il s'est donc dégagé au pôle positif un corps agissant sur le liège avec une activité toute différente de celle de l'acide fluorhydrique.

Je dois ajouter qu'afin de diminuer la tension de vapeur de l'acide fluorhydrique, nous avons refroidi ce liquide dans nos expériences au moyen du chlorure de méthyle, qui, par une rapide évaporation, nous produit un froid de  $-50^{\circ}$  (centigrade).

Il a fallu modifier l'appareil et particulièrement la fermeture du tube en U. Les bouchons en fluorine à frottement doux ne m'ont pas donné de bons résultats. La gomme laque ou la gutta-percha dont on les entourait était rapidement attaqué par le corps gazeux produit au pôle positif. On dut alors recourir à une fermeture gazeuse, au moyen de pas de vis en platine, et voici après bien tâtonnements, comment l'expérience fut disposée.

Le tube en U en platine est fermé par des bouchons à vis. Chacun de ces bouchons est formé par un cylindre de spath-fluor, bien serti dans un cylindre creux de platine, dont l'extérieur porte le pas de vis. Chaque bouchon de fluorine laisse passer en son axe une tige carrée de platine. Ces tiges, plongeant par leur extrémité inférieure dans le liquide, servaient d'électrodes. Enfin, deux ajutages en platine soudés à chaque branche du tube, au-dessous des bouchons, par conséquent au-dessus du niveau du liquide, permettaient aux gaz dégagés par l'action du courant de s'échapper au dehors.

Pour obtenir l'acide fluorhydrique pur et anhydre on commence par préparer le fluorhydrate de fluorure de potassium en prenant toutes les précautions indiquées par Fremy. Lorsqu'on a obtenu ce sel pur, on le dessèche au bain-marie à  $100^{\circ}$ , et la capsule qui le contient est placée ensuite dans le vide en présence d'acide sulfurique concentré et de potasse fondue au creuset d'argent. L'acide et le potasse sont remplacés tous les matins pendant quinze jours et le vide est toujours maintenu dans les cloches à 1 centim. de mercure environ.

Il faut avoir soin pendant cette dessiccation, de pulvériser le sel de temps en temps dans un mortier de fer, afin de renouveler les surfaces ; lorsque le fluorhydrate ne contient plus d'eau, il tombe en poussière

et peut alors servir à préparer l'acide fluorhydrique. Il est à remarquer que le fluorhydrate de fluorure de potassium bien préparé est beaucoup moins déliquescent que le fluorure.

Lorsque le fluorhydrate est bien sec, il est introduit rapidement dans un alambic en platine que l'on a séché en le portant au rouge peu de temps auparavant. On le maintient à une douce température pendant une heure ou une heure et demie de façon que la décomposition commence très lentement; on perd la première portion d'acide fluorhydrique formé qui entraîne avec elle les petites traces d'eau pouvant rester dans le sel. Le récipient de platine est alors adapté à la cornue et l'on chauffe plus fortement, tout en conduisant la décomposition du fluorhydrate avec une certaine lenteur. On entoure ensuite ce récipient d'un mélange de glace et de sel, et à partir de ce moment, tout l'acide fluorhydrique est condensé et fournit un liquide limpide, bouillant à  $19^{\circ} \cdot 5$ , très hygroscopique et produisant, comme l'on sait, d'abondantes fumées en présence de l'humidité de l'air.

Pendant cette opération, le tube en U en platine, desséché avec le plus grand soin, a été fixé au moyen d'un bouchon dans un vase de verre cylindrique et entouré de chlorure de méthyle. Jusqu'au moment de l'introduction de l'acide fluorhydrique, les tubes abducteurs sont reliés à des éprouvettes desséchantes contenant de la potasse fondue. Pour faire pénétrer l'acide fluorhydrique dans ce petit appareil, on peut l'absorber par l'un des tubes latéraux dans le récipient même où il s'est condensé.

Lorsqu'on a fait pénétrer, à l'avance, un volume déterminé d'acide fluorhydrique liquide dans le petit appareil en platine, refroidi par le chlorure de méthyle en ébullition tranquille, à la température de  $-23^{\circ}$ , on fait passer dans les électrodes le courant produit par 25 éléments Bunsen, grand modèle, montés en série. Un ampèremètre, placé dans le circuit, permet de se rendre compte de l'intensité du courant.

Afin de rendre l'acide conducteur, nous y avons ajouté, avant l'expérience, une petite quantité de fluorhydrate de fluorure de potassium séché et fondu; environ 2 grammes pour 10 centimètres cubes d'acide. Dans ce cas, la décomposition se produit d'une façon continue, et l'on obtient, au pôle négatif, un gaz brûlant avec une flamme incolore et présentant tous les caractères de l'hydrogène; au pôle positif, un gaz incolore d'une odeur pénétrante très désagréable, se rapprochant de celle de l'acide hypochloreux, et irritant rapidement la muqueuse de la gorge et les yeux. Nous faisons en ce moment l'expérience sous vos yeux. Le nouveau corps gazeux est doué de propriétés très énergiques: vous voyez le soufre s'enflammer à son contact.

Le phosphore prend feu et fournit un mélange d'oxyfluorure et de fluorure de phosphore. L'iode s'y combine avec une flamme pâle en perdant sa couleur. L'arsenic et l'antimoine en poudre se combinent au fluor avec incandescence.

Le silicium cristallisé, froid, brûle de suite au contact de ce gaz

avec beaucoup d'éclat. Parfois il se produit des étincelles ; il se forme du fluorure de silicium qui a été recueilli sur le mercure et nettement caractérisé.

Le bore pur brûle également en se transformant en fluorure de bore. Le carbone amorphe devient incandescent au contact du fluor. Pour faire ces différentes expériences, il suffit de placer, comme vous le voyez, les corps solides dans un petit tube de verre et de les approcher de l'extrémité du tube de platine par lequel se dégage le fluor. On peut aussi répéter ces expériences en mettant de petits fragments des corps solides à étudier sur le couvercle d'un creuset de platine maintenu auprès de l'ouverture du tube abducteur.

Ce gaz décompose l'eau à froid en fournissant de l'acide fluorhydrique et de l'ozone ; il enflamme le sulfure de carbone et, recueilli dans une capsule de platine remplie de tétrachlorure de carbone, il fournit un dégagement continu de chlore.

Le chlorure de potassium fondu est attaqué à froid, avec dégagement de chlore. En présence du mercure, l'absorption est complète avec formation de protofluorure de mercure de couleur jaune clair. Le potassium et le sodium deviennent incandescents et fournissent des fluorures. D'une façon générale, les métaux sont attaqués avec beaucoup moins d'énergie que les métalloïdes. Cela tient, pensons-nous, à ce que la petite quantité de fluorure métallique formé empêche l'attaque d'être profonde. Le fer et le manganèse en poudre brûlent en fournissant des étincelles.

Les corps organiques sont violemment attaqués. Un morceau de liège, placé auprès de l'extrémité du tube de platine par lequel le gaz se dégage, se carbonise aussitôt et s'enflamme. L'alcool, l'éther, la benzine, l'essence de térébenthine, le pétrole prennent feu à son contact.

En opérant dans de bonnes conditions on peut obtenir à chaque pôle un rendement de 2 litres à 4 litres de gaz par heure.

Lorsque l'expérience a duré plusieurs heures et que la quantité d'acide fluorhydrique liquide restant au fond du tube n'est plus suffisante pour séparer les deux gaz, ils se recombinaient à froid dans l'appareil en platine, avec une violente détonation.

Nous nous sommes assurés par des expériences directes, faites au moyen d'ozone saturé d'acide fluorhydrique, qu'un semblable mélange ne produit aucune des réactions décrites précédemment. Il en est de même de l'acide fluorhydrique gazeux. Nous ajouterons que l'acide fluorhydrique employé ainsi que le fluorhydrate de fluorure étaient absolument exempts de chlore. Enfin, on ne peut pas objecter que le nouveau gaz produit soit un perfluorure d'hydrogène ; car en présence de fer chauffé au rouge maintenu dans un tube de platine, il est absorbé entièrement sans dégagement d'hydrogène.

Enfin, dans des recherches plus récentes je me suis assuré qu'il est possible de faire ces expériences dans un appareil de cuivre tel que celui que vous avez devant vous.

Par l'électrolyse de l'acide fluorhydrique rendu conducteur au



moyen de fluorhydrate de fluorure de potassium, on obtient donc au pôle négatif de l'hydrogène et au pôle positif un dégagement continu d'un corps gazeux présentant des propriétés nouvelles, doué d'affinités très énergiques : ce corps gazeux est le fluor.

Nous avons pu en déterminer la densité, la couleur, le spectre, étudier son action sur les corps simples et composés.

Maintenant que l'on connaît les principales propriétés du fluor, maintenant que cet élément a pu être isolé, je suis convaincu que l'on trouvera, malgré l'énergie de ses réactions, de nouvelles méthodes de préparation.

Il est à croire que l'on arrivera à préparer le fluor par un procédé chimique fournissant de meilleurs rendements que le procédé électrolytique.

Le fluor aura-t-il jamais des applications ?

Il est bien difficile de répondre à cette question. D'ailleurs, je puis le dire en toute sincérité, je n'y pensais guère au moment où j'ai entrepris ces recherches, et je crois que tous les chimistes qui ont tenté ces expériences avant moi n'y pensaient pas davantage.

Une recherche scientifique est une recherche de la vérité, et ce n'est qu'après cette première découverte que les idées d'application peuvent se produire avec utilité.

Il est évident que lorsqu'on voit les grandes transformations industrielles qui se font aujourd'hui sous nos yeux, on ne peut se prononcer sur cette question. Après la préparation de l'acier Bessemer, la fabrication du manganèse au haut fourneau, la production de l'alizarine de synthèse, le chimiste hésite toujours à nier la vitalité industrielle d'une réaction de laboratoire.

Quand on pense à la valeur qu'avaient certains métaux tels que le potassium et le sodium, lorsque Davy les préparait par électrolyse ; quand on se rappelle que, par le procédé de Gay-Lussac et Thénard, ils revenaient à quelques milliers de francs le kilogramme, et qu'aujourd'hui par les méthodes électrolytiques ils ne coûtent plus que 5 francs, on n'ose plus dire qu'une réaction chimique ne saurait avoir d'applications industrielles.

Seulement, messieurs, et c'est par là que je termine, il est curieux de voir combien il faut d'efforts continus, de vues différentes, pour arriver à résoudre une de ces questions scientifiques ; je devrais dire plutôt pour faire progresser une de ces questions scientifiques, car en réalité un sujet n'est jamais fermé. Il reste toujours ouvert pour nos successeurs : nous ne faisons qu'ajouter un anneau à une chaîne sans fin.

L'avancement de la science est lent ; il ne se produit qu'à force de travail et de ténacité. Et lorsqu'on est arrivé à un résultat, ne doit-on pas par reconnaissance se reporter aux efforts de ceux qui vous ont précédés, de ceux qui ont lutté et peiné avant vous ? N'est-ce pas en effet un devoir de rappeler les difficultés qu'ils ont vaincues, les vues qui les ont dirigés et comment des hommes, différents de pays et d'idées, de position, et de caractère, mus seulement par l'amour de

la science, se sont légués sans se connaître la question inachevée ; afin qu'un dernier venu pût recueillir les recherches de ses devanciers et y ajouter à son tour, sa part d'intelligence et de travail ? Collaboration intellectuelle entièrement consacrée à la recherche de la vérité et qui se poursuit ainsi de siècle en siècle.

Ce patrimoine scientifique que nous cherchons toujours à étendre est une partie de la fortune de l'humanité ; nous devons garder un souvenir reconnaissant à tous ceux qui lui ont donné la chaleur de leur cœur et le meilleur de leur esprit.

[H. M.]

Friday, February 25, 1898.

SIR FREDERICK ABEL, Bart. K.C.B. D.C.L. LL.D. F.R.S.  
Vice-President, in the Chair.

CAPTAIN ABNEY, C.B. D.C.L. F.R.S. M.R.I.

*The Theory of Colour Vision applied to Modern Colour Photography.*

THE subject of my address this evening is a very large one, and would occupy more time than the hour allotted to me, if I entered fully into every part of it. All I can hope to do is to put before you the main scientific reasoning which has led to the success at present attained in colour photography, by a combination of colours, and by the absorption of colouring matter.

On the screen we have the spectrum of the electric light, and a very beautiful object it is. But it is not to its beauty that I wish to call your attention, but to the varying brightness of its different parts, and further, to the fact that in it we have strictly pure colours, that is a series of simple colours, and not mixed colours such as we may find in nature. Now if we can reproduce fairly well by means of photography this grand multi-coloured band, both as regards colour and also brightness (that is luminosity), we may say that we have succeeded in doing what is required, and that all hues in nature, with their varying shades and brightness, can be equally well reproduced. The exponent of colour photography is bound to go to the spectrum for his information, and this I must do to-night. On the wall is a diagram of the spectrum in the shape of a curve, which shows the luminosity of every individual part. If we could abolish colour from our minds, and merely look upon the spectrum as a monochromatic band having waves of different oscillation frequency, we should have this same curve, and our eyes would be like a photographic plate, which knows no colour quâ colour. All that the plate knows is that a certain wave length, having a certain amplitude, will so affect its sensitive surface that a certain opacity of deposit will be attained on applying the developer to it. If two or more colours are mixed, each of the wave lengths will play its own part, and an opacity will be produced representing the sum of the separate effects. A little reflection will show that whatever photographs we may obtain we must use outside coloured light to illuminate them if a coloured object is to be reproduced. We have to consider what are the fewest

This concentration or focussing of the cathode rays by means of a magnetic field, which has been studied by Birkeland and by Fleming, can be also shown by means of another tube, the interior of which is free from any obstruction. This tube, when excited in the ordinary manner, shows, as you will observe, the usual green fluorescence nearly all over its surface, but especially at the rounded end opposite the cathode. I suspend this tube over one pole of a powerful electro-magnet, placed with its axis in line with that of the tube as shown in Fig. 1. As more and more electric current is passed round the electro-magnet, and the magnetic field becomes stronger and stronger, it will be observed that the beam of cathode rays becomes more and more concentrated to a point opposite the pole of the magnet, until at length when the magnet is fully excited the whole of the green fluorescence in the tube has now entirely died out, and the cathode stream can be seen as a bluish cone, the base of which is the cathode disc, and the apex is a very small point exactly over the centre of the magnet pole. It is not possible to keep the tube in this condition for more than a few seconds, as the heat produced on the glass where the cathode rays are concentrated is so intense as to quickly perforate the latter. Indeed, by slowly moving the tube it is possible to engrave on its interior surface any desired figure, the action of the cathode rays being sufficient to erode the glass. Fig 2 is a photograph of the globular end of a tube, upon the interior glass surface of which, as can be seen, a square with diagonals has been roughly engraved by this means.

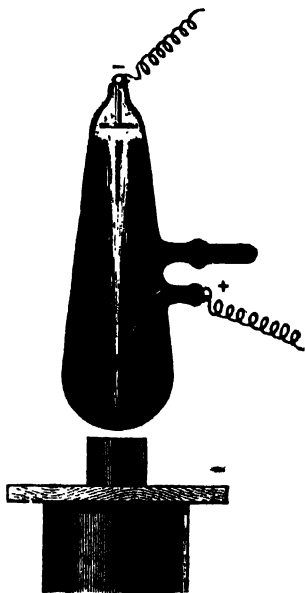


FIG. 1.—Cathode rays focussed to a point by means of a magnet.

Whether the action is due directly to the bombardment of the atoms which form the cathode rays breaking off little pieces of glass as a volley of minute bullets would do, or whether it is a secondary effect due to heat, is perhaps uncertain. The result in any case is that where the concentrated cathode rays impinge upon the glass, the latter is eroded and visibly roughened.

A concentrated cathode discharge can also be obtained by employing as cathode a spherically concave aluminium cup, so arranged relatively to the glass of the tube that the rays are given off only from the hollow side, this being the arrangement now universally used in tubes for the production of the Röntgen rays. It is a method origi-

nally introduced by Crookes, more especially for showing the heating effect of the cathode rays when allowed to impinge upon a piece of platinum foil, and it is to Herbert Jackson that we owe its application to the production of the Röntgen rays.

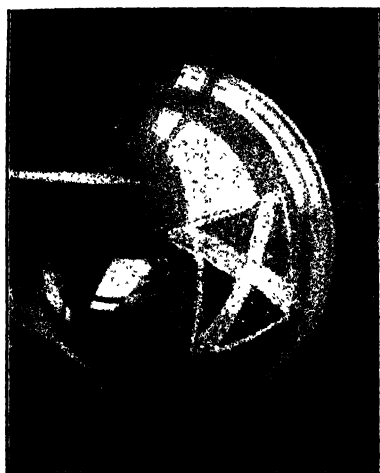


FIG. 2.—Figure engraved on the interior of a glass bulb by cathode rays.

Here is a tube arranged as in Fig. 3 with two concave cathodes opposite one another, both focussing upon a small fragment of quicklime. I employ in this case two cathodes because I am going to use an alternating electric current, such as is supplied from the mains, but transformed up to some 20,000 volts by being passed through an induction coil. Each aluminium cup serves in turn as cathode and anode, and, as will be observed, when the current is turned on and conditions are favourable, a very brilliant and beautiful light is produced. This, however, only lasts for a short time and then dies out, the strong light recurring from time to time at unequal intervals. This curious effect, which in result is analo-

gous to the hunting of a badly adjusted arc lamp, requires explanation. It appears to be due to absorption of the residual gas by the lime while the latter is white hot, and the giving of it out again at a lower temperature; this producing a periodic increase and decrease of the vacuum, and a consequent decrease and increase of the energy of the discharge through the tube and of the light. Another curious fact, and one that supports the bombardment theory of the cathode rays, is that the rays after having been allowed to fall upon the block of lime for a little time, are found to bore perfectly straight and very minute holes in the material. This block, which has been used on several occasions, and has also been turned round a little, was solid originally, but has now several holes passing right through it, some of these not being more than about half a millimetre in diameter. At the edges the material is somewhat broken away, but in the interior the holes have been so accurately eroded by the cathode rays that they look as though they might have been bored with a small drill. This shows the great accuracy with which the cathode rays can be focussed. Again, it is remarkable that though the current is alternating, and the arrangement of the tube and electrodes perfectly symmetrical, so that one would expect the heating and luminous effect

on both sides of this piece of lime to be the same, the light appears to be given off sometimes only on one side and sometimes only on the other.

With a tube such as this, excited with an alternating current, it is easy to produce exceedingly high temperatures confined to a very small

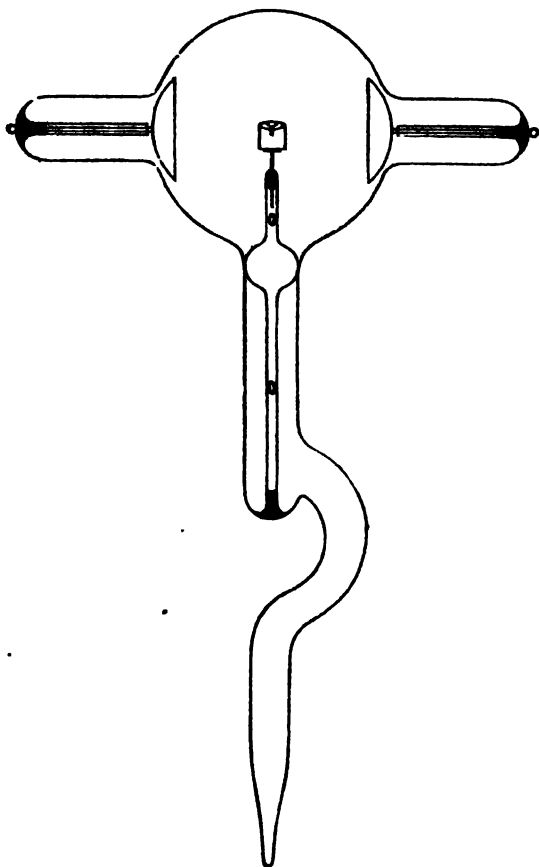


FIG. 3.—Cathode ray lamp.

area, and it is not at all improbable that it may be eventually found possible to produce commercially and practically in this way, high voltage electric lamps of much higher efficiency than the ordinary incandescent filament lamp, and possibly even rivalling arc lamps. In both of these latter it is necessary that the incandescent substance

should be a fairly good electrical conductor ; whereas in this cathode ray arrangement there is no such limitation, and consequently there is a much wider range of available refractory substances. It is also quite conceivable that in future an electric furnace of this nature may be found of service in some of the more delicate of chemical investigations where it is necessary to obtain in isolated substances very high temperatures. Indeed, already Crookes and Moissan have employed this means for turning into graphite the surface of a diamond.

It is now becoming more and more generally believed that Sir William Crookes' original theory, enunciated some twenty years ago, as to the nature of these cathode radiations, is at any rate to a large extent correct. According to this theory the cathode rays consist of material particles of the residual gas, which being similarly electrified by contact with the cathode are violently repelled by the latter. This has been the view held for a long time by most English physicists, and the chief point of difference now appears to be whether these material particles are single atoms, single molecules, or larger aggregations of matter.

I have here a model which roughly shows what is supposed to take place. As you see, there are facing one another two plate electrodes, which I am able to charge positively and negatively respectively by means of a Wimshurst machine ; between them is suspended by a silk thread, what for the moment we will assume to be a single atom. It is in fact a gilded pith ball. As soon as I turn the handle of the Wimshurst machine and electrify the electrodes, as you see, the ball oscillates rapidly from one to the other. If it starts in contact with the negative electrode it receives from this a negative charge ; it thereupon is repelled until it strikes the positive electrode, where it gives up its negative charge and receives a positive one. Again, owing to mutual repulsion, it is driven across to the negative electrode, and so on backwards and forwards. This is a very simple and elementary experiment, which I would not have ventured to show you except that it leads to another which is perhaps of more interest. If the atoms in a tube were caused to fly backwards and forwards at equal velocities, as did the pith ball, between anode and cathode, it is obvious that there would be an anode stream similar in most if not in all respects to the cathode stream, which does not appear to be the case. If, however, I now remove the connection between the positive electrode and the Wimshurst machine, and instead, connect the positive electrode to earth, leaving the negative electrode connected to the Wimshurst machine as before, it will be seen that the pith ball flies with much greater violence and rapidity from cathode to anode than it does on its return journey from anode to cathode. This is for the reason that while in the former case we have both the repulsion of the cathode on the similarly electrified ball and also the attraction of the anode urging the ball on its path, on the return journey both ball and anode are at zero potential, and consequently there is the attraction of the distant cathode only causing the ball to move. Now, if we

consider the condition of affairs inside a focus tube while a discharge is taking place, this last experiment may help us to understand at least one possible reason for the atoms not being projected from the anode at anything like the velocity that they are projected from the cathode.

Fig. 4 has been prepared to show the probable distribution of positively and negatively electrified atoms in a focus tube while the discharge is taking place. It is largely based upon previous similar illustrations due to Crookes, applied to a tube of a different form. As will be seen, the greater portion of the bulb is filled with positively electrified atoms, as denoted by crosses, while it is only behind the cathode and in the cathode stream itself that any negatively electrified atoms are to be found. That this is at any rate approximately true can be proved by means of exploring poles and in other ways, and it is curious to note that some of the very beautiful photographs published by Lord Armstrong in his recent monograph on 'Electric Movements in Air and Water' show that in air at ordinary atmospheric pressure there is a similar tendency for the positive discharge to be much more dispersive than the negative.

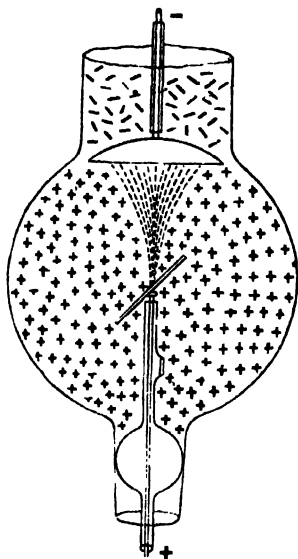


FIG. 4.—Diagram showing probable distribution of positively and negatively charged atoms in a focus tube.

Now assuming that the figure correctly denotes the condition of the atoms inside the tube, it is evident that considering only the contents of the tube and disregarding everything outside, the anode is very much in the same condition as the earthed electrode in the pith ball experiment; being at the same electrical potential as the great bulk of its environment. It is very probably for a similar reason that in a tube of the form illustrated the cathode rays are only given off from the concave side of the cathode, the whole environment of the convex side being negatively charged, with the result that the atoms there are in a state of equilibrium.

Whether this explanation is sufficient or not—and no doubt there are at work other causes—in any case there is no question that the velocity of the negative stream is very much greater than the velocity of the positive stream. That there is something of the nature of a positive stream, which increases in velocity the higher the exhaustion, can, however, be shown experimentally.



Fig. 5 is a radiometer tube, exactly similar in principle to those of Crookes. It consists of an ordinary focus tube, on one side of which a glass annex has been blown, containing a sliding carrier, holding half inside a glass cup a small and delicately pivoted wheel with mica vanes. By the employment of a magnet, which acts on a piece of iron attached to the sliding carrier inside the tube, I can move the wheel bodily, either out into the centre of the tube, so that the cathode stream impinges upon the vanes, or back into the annex, where the cathode stream is turned on the glass cup.

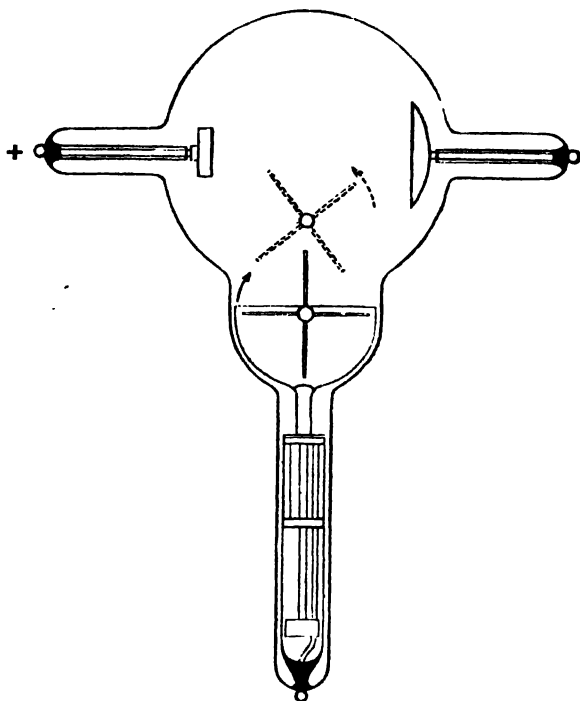


FIG. 5.—Adjustable radiometer tube for showing both cathode and anode streams.

when the vanes are quite outside of the cathode line of fire. When the tube is put into operation in this latter position (that shown in full lines in the illustration), immediately the current is turned on the wheel begins slowly to revolve in a direction that indicates a stream from the anode to the cathode. On the other hand, when the wheel is moved out into the bulb (in the position indicated in dotted lines), so that the cathode stream impinges upon the vanes, the wheel immediately begins to revolve with great rapidity in the opposite direction.

Here, therefore, we have direct experimental evidence that in a focus tube, while the cathode stream of negatively electrified atoms proceeds at a great velocity through the centre of the bulb, the anode stream of positively electrified atoms returns to the cathode at a much lower velocity round the outside of the cathode stream. Fig. 6 shows approximately what probably occurs in a tube of the ordinary focus type, the direction of the two opposite streams of positively and negatively charged atoms being shown by the arrow-heads.

If the discharge within a focus tube be closely watched during the process of exhaustion, it will be found to alter as the vacuum increases. First of all, at a low vacuum, the cathode rays can be seen converging in the form of a cone from the concave cathode to a focus, and then immediately diverging again in another cone on the other side of the focus, as shown on the extreme left of Fig. 7. It can further be shown that the individual rays cross at the focus. As the exhaustion proceeds, both convergent and divergent cones, but especially the latter, become smaller and smaller, while the thread that joins them becomes longer and longer as shown in the succeeding sections of Fig. 7, till at last, at the highest vacuum at which the discharge will pass, the cathode rays, which are now very nearly invisible, appear to come off only from a small area at the centre of the cathode, and not very appreciably to diverge again after once having come together, as indicated on the extreme right of the illustration.

Now I have found that if the anti-cathode or anode upon which the cathode rays impinge is made not of aluminium or of platinum as usual, but of ordinary electric light carbon, the carbon becomes luminescent where struck by the rays. Further, if the carbon anti-cathode be so placed as to intersect either the convergent or divergent cones of rays, these, instead of producing a uniform luminous patch upon the carbon, produce a bright ring with a dark interior. This ring becomes smaller as the vacuum is increased. It develops a bright spot in the centre as exhaustion proceeds still further, and finally with a still higher vacuum it closes round the spot until only the spot itself is left. These effects are shown for each condition of vacuum in the lower portion of Fig. 7, and I have here a tube that I

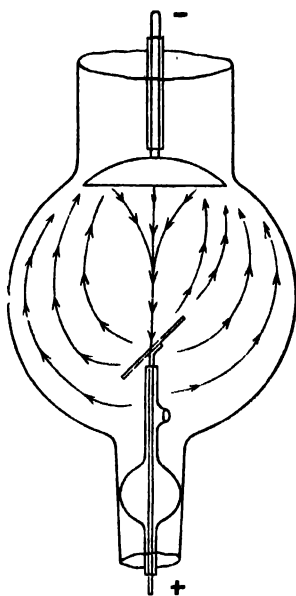


FIG. 6.—Diagram showing probable circulation of atoms in a focus tube.

will put into action and show the effect for one degree of vacuum. As you observe, the luminescence on the carbon is very bright, in fact the surface appears white hot. It, however, takes the shape of a well defined hollow ring with a dark interior and a bright spot at the centre, and as I deflect the stream of cathode rays with a magnet, the ring also moves with no perceptible lag, being at the same time somewhat deformed, but still retaining its hollow character.

By means of a tube in which the carbon anti-cathode is connected to the positive terminal by sliding connections, and can be caused to move along the tube so as to intersect either the convergent or di-

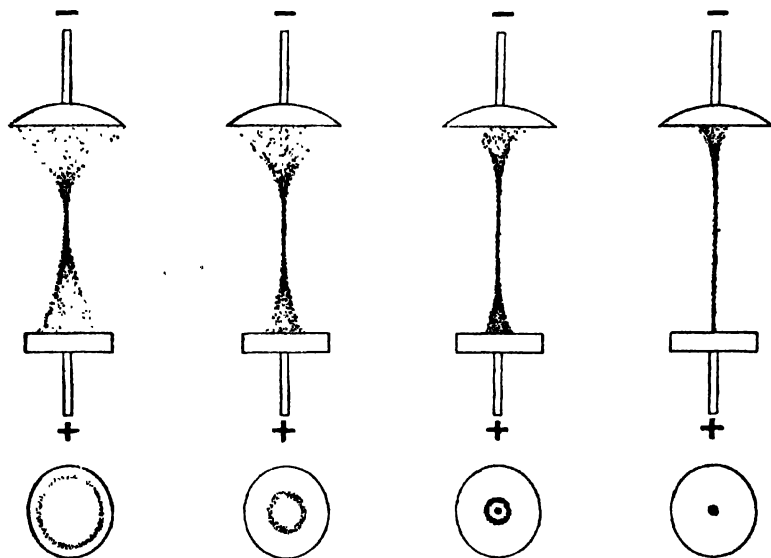


FIG. 7.—Appearance and effect of the cathode rays in a focus tube at four different degrees of exhaustion.

vergent cones at any desired point, it can be shown that with cathodes of considerable concavity, both the convergent and divergent cones of cathode rays are never solid but always more or less hollow in section.

Now, how can this remarkable effect be explained? Perhaps the most satisfactory explanation is that suggested by Professor G. F. Fitzgerald, which accords with the Crookes theory of cathode rays, and also with what I have already mentioned as to the anode stream of positively charged atoms returning to the cathode outside of the cathode stream passing in the opposite direction. If we return to Fig. 6, it is evident that the supply of atoms to the active cathode

surface is from all round the edge of the latter, so that the atoms may very possibly be all shot off again from the cathode in the form of a hollow cone before they get further than a certain distance towards the centre. Further, as the vacuum increases we know from our experiments with our radiometer tube that the velocity of the positive stream also increases very considerably, so that under the conditions of a higher vacuum the atoms approaching the cathode have more momentum and consequently get nearer to the centre before they obtain a negative charge and are repelled in the cathode stream, thus making the stream and the rings smaller in diameter. Of course, once we start with a hollow convergent cone it is easy to understand that the divergent cone will also be hollow, seeing that the atoms fly more or less rectilinearly crossing one another's paths at the focus. How to explain the bright spots in the centres of the rings, which appears to indicate a central negative stream down the axis of the hollow cones, is more difficult, but possibly the heterogeneous nature

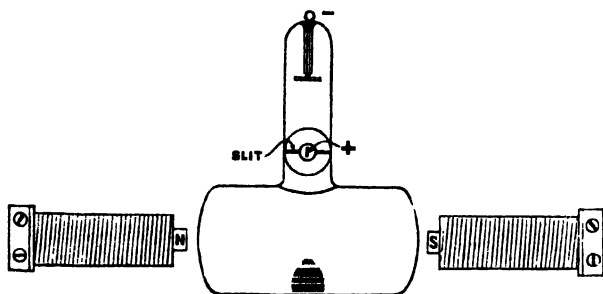


FIG. 8.  
Apparatus for showing the cathode ray spectrum.

of the cathode stream, due very probably to the varying velocities of the negatively charged atoms, may be sufficient to account for this.

Crookes observed many years ago that cathode rays were deflected by a magnet. Lenard was the first to show that the rays are not homogeneous, but some are more easily deflected than others. Birke-land went one step further than this, and showed that if a thin cathode beam was deflected by a suitable magnetic field it was split up into bundles of rays, and if allowed to fall upon the glass walls of the tube, it gave fluorescent bands of alternate brightness and darkness, which he termed the magnetic spectrum.

Fig. 8 represents an apparatus for showing this effect. The cathode rays proceeding from a flat aluminium disc are caused to pass through a narrow slit in a piece of platinum which serves as the anode. After passing through the slit, the rays impinge upon the bulb, and if otherwise unaffected, produce a narrow band of intense luminescence upon the glass. At each side of the bulb is

fixed an electromagnet, producing straight magnetic lines across the path of the rays. As soon as the magnets are excited the cathode beam is deflected and split up, and instead of having a single narrow line of luminescence, we now have many lines with dark intervening spaces, all in constant movement. An experiment like this cannot be shown to an audience, but I have prepared photographs which will make the effect produced clear. Fig. 9 is a photograph taken without camera or lens, and produced simply by binding a strip of sensitive photographic film round the bulb of the tube and making a single discharge by a single break of the contact-breaker of the induction coil. The film being in close contact with the glass is impressed by the luminous bands that the unequally deflected cathode rays produce on the latter, and we have a photographic image of the bands for a single electrical discharge. Nor is this all. By inserting between the glass and the photographic film a piece of very thin black paper, so placed as to cover only one-half of the spectrum, it is possible to obtain a photograph of the bands, one half of which is due to the visible fluorescent luminosity of the glass, and the other half to the invisible Röntgen rays produced by the impact of the cathode rays on the glass.

Fig. 10 is such a photograph, and it will be seen that the Röntgen rays are also given off in bands, which are co-terminous with the fluorescent bands though photographically fainter than the latter. In the photographs shown, this difference in density between the two images is lessened by the interposition between the glass and the film in the case of the luminous portion of a thin sheet of slightly yellow celluloid. Without this the difference would be so great that it would not be possible to show both images upon a single film. Of course, this faintness of the Röntgen ray bands is only to be expected, as in the photograph of the luminous bands the Röntgen rays are also present, so that in the one case the photographic image is the result of both descriptions of radiations, and in the other is caused by only one. It is worthy of note that in the spectrum image produced by the Röntgen rays, the greatest photographic effect is always produced by the least deflected of the cathode ray streams, that is to say, by that stream which presumably was travelling at the greatest velocity. It is obvious that the cathode ray atoms which are travelling most rapidly will be the ones least deflected, just as the faster is the flight of a bullet the flatter is its trajectory. Here we have a probable explanation of the existence of the bands which most likely are due to the atoms of the cathode rays having either from the first different velocities imparted to them, due to the oscillatory character of the induction coil discharge, or from their gathering into groups travelling at different velocities on the well-known principle that occasions the traffic in the street to form knots of maxima and minima, owing to the faster vehicles catching up the slower and being impeded by them.

The axial stream in the centre of the hollow cathode ray cones may possibly also be due to the same cause.

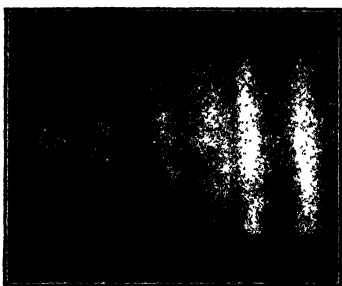


Fig. 9.

Cathode ray spectrum image photographed directly by the visible fluorescent radiations. <sup>4</sup>

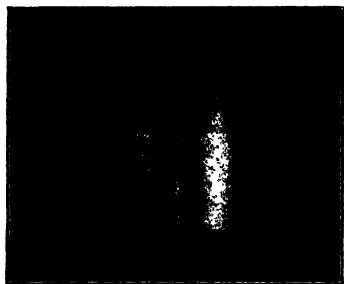


Fig. 10.

Cathode ray spectrum image photographed, one half by the visible radiations, and one half by the invisible Röntgen radiations.

In any case the photographs that I have shown you prove very conclusively that those negative atoms which are least deflected by a magnet are those which produce the most active Röntgen rays, and therefore it follows that the quality of the Röntgen rays is very largely dependent upon the velocity with which the negative atoms strike upon the anti-cathode. Quite in harmony with this theory is an experiment which I will now show you. I have here a Röntgen ray tube with two cathodes, as shown in Fig. 11. The cathodes are both in the same tube, and therefore the conditions as regards vacuum must be the same for both. They both focus upon opposite sides of the same platinum anti-cathode, and they only differ in the fact that

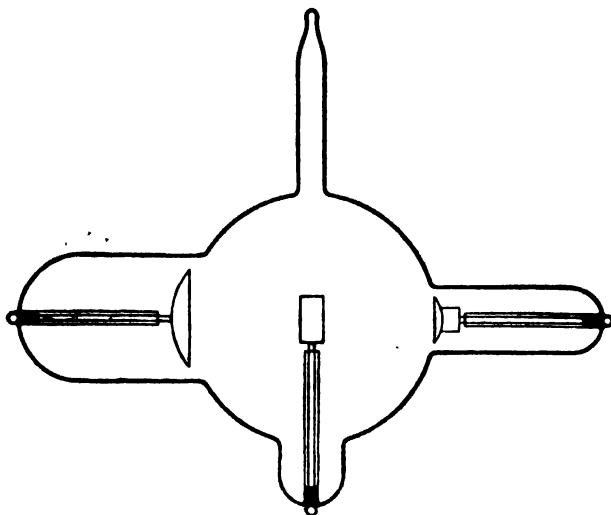


FIG. 11.

Focus tube with two cathodes of different diameters.

one is considerably larger than the other. I will now put the tube into operation, using the larger cathode, and as you see, scarcely any Röntgen rays are produced, while what there are do not penetrate my hand. I will now alter the connections and use the smaller cathode instead of the larger one. Now very penetrative Röntgen rays are generated in abundance, and you can clearly see the shadow of the bones in my hand on the fluorescent screen.

Here is another tube which is furnished with four cathodes all of different sizes and all arranged to focus upon the same anti-cathode, which can be rotated so as to face the particular cathode in use. This tube behaves just like the other, and for any given degree of exhaustion gives more penetrative Röntgen rays the smaller the cathode employed.

It is found that the smaller the cathode the greater is the E.M.F. required to cause the electric discharge to pass through the tube, and probably in consequence of this, and also perhaps because a less number of atoms can get into the vicinity of the cathode at one time, the greater is in all probability the velocity of the stream of atoms that form the cathode rays.

The particular material employed for the anti-cathode surface also materially affects the production of the Röntgen rays. This is a subject that was, I believe, first investigated by Professor Silvanus Thompson, who found that the best absorbents were the best emitters of the Röntgen rays—in other words, that the best materials for the anti-cathode were metals of the highest atomic weight. If the Röntgen rays are produced by the sudden removal of velocity from the cathode ray atoms, or by a sudden change in this velocity by collision with the atoms of the anti-cathode, this is in accordance with what would be expected, as substances of high atomic weight would obviously be the most efficient by reason of the greater inertia of their atoms.

I have made numerous experiments with various metals for the anti-cathode, and I have here a tube which has a movable anti-cathode made half of aluminium and half of platinum. By jerking the tube, either the platinum or the aluminium portions can be brought opposite the cathode and put into use, so that under exactly similar conditions as regards vacuum, size of cathode and bulb and distance, it is possible accurately to compare the efficiency of the two substances. Fig. 12 is a photograph of my wrist taken with the platinum portion of the anti-cathode, and Fig. 13 one taken with the aluminium portion. The conditions were otherwise identical, but, as is very obvious, the result with the platinum is much superior to the other.

The usual method adopted for varying the resistance of a Röntgen ray tube, and thus modifying the character of the Röntgen rays that it produces, so as to obtain the exact penetrative quality that is desired, is by varying the vacuum. The higher the exhaustion the greater is the resistance to the passage of the discharge, the greater is the velocity of the cathode rays, and the more penetrative are the Röntgen rays. This variation of the vacuum is usually effected by heating the tube, which has the effect of driving out into the interior molecules of the residual gas condensed or occluded upon the glass. Apart from this, very possibly the temperature of the contents of the tube and the kinetic energy of the molecules, which is greater the higher the temperature, may in itself assist the passage of the discharge.

There are, however, other means of varying the resistance of a tube and altering the character of the rays that it generates which do not depend upon either the degree of exhaustion or upon the temperature. One method for effecting this regulation consists in making the anti-cathode, which is also the anode, movable, and altering the distance between it and the cathode; another in making the cathode movable and altering its position relative to the glass walls of the tube.





FIG 12.  
PLATINUM.



FIG. 13.  
ALUMINIUM.

Photographs showing relative results obtained with anti-cathodes of platinum and aluminium.

In the former case the tube may be constructed as shown in Fig. 14, in which the anti-cathode is mounted on a sliding stem so that by

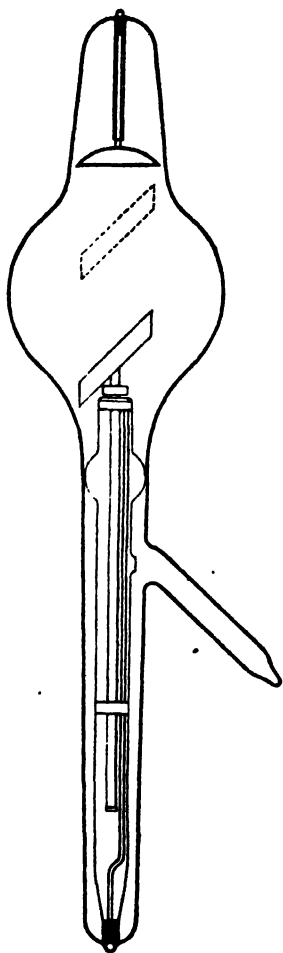


FIG. 14.  
Adjustable anode tube.

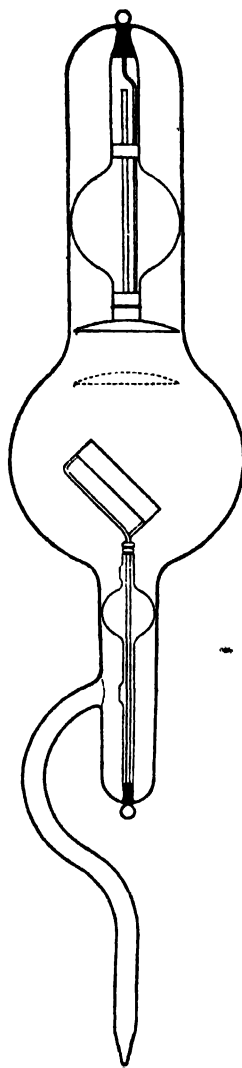


FIG. 15.  
Adjustable cathode tube.

shaking the tube its distance from the cathode can be varied. In this case the nearer the anti-cathode is placed to the cathode the higher is the resistance of the tube and the more penetrative are the Röntgen rays that are generated.

Fig. 15 shows another form of adjustable tube in which the anti-cathode is stationary, and it is the cathode that is movable. The cathode is here so mounted upon a sliding stem that it can be moved in and out of a slightly conical annex blown upon one side of the glass bulb of the tube. I will put a tube of this description into operation, beginning with the cathode in the position shown in the illustration in dotted lines, when it is outside the annex in the bulb, and let you see the effect of gradually moving it backwards into the annex. We will observe the character of the resulting Röntgen rays produced at each position with a fluorescent screen. The tube used has a small piece of iron attached to the cathode so that we can move the latter by means of a magnet according to the suggestion of Dr. Dawson Turner and others.

You observe that, to commence with, with the cathode right out in the bulb we get Röntgen rays which can do little more than penetrate the black paper backing of the screen. My hand throws a dark shadow on the fluorescent surface, but you can see no bones, as the rays will not penetrate my hand. I now move the cathode a little back towards the edge of the annex. The bones are now just visible. The hand is still very black, but the bones can be seen; now on moving the cathode just inside the edge of the annex the bones become very clear, and when I move it still further into the annex the rays become very penetrative, and even pass through the bones so that their structure can be observed.

Figs. 16, 17 and 18 show a series of three photographs of my hand obtained in this manner. They were all taken with the same tube under identical conditions as regards vacuum, distance, exposure, photographic plate and development. The position of the cathode only was altered, and, as will be observed, the results show a marked increase of penetration the further the cathode was moved towards and into the glass annex. In the case of Fig. 16 the cathode was right out in the bulb, in Fig. 18 it was completely in the annex. In Fig. 17 it was in an intermediate position.

Now we have studied the cause of these effects by means of a tube in which positions of both anode and cathode can be altered independently by a magnetic adjustment. Fig. 19 shows a portion of the tube, and above it is drawn a curve representing approximately the difference of potential required to cause a discharge to pass through the tube with varying positions of the anti-cathode. In the diagram the abscissæ represent the distance between anti-cathode (which also formed the anode) and the cathode, divided in tenths of an inch, while the ordinates represent also in tenths of an inch the length of the alternative sparks in air between two brass balls  $\frac{3}{4}$  inch in diameter. Starting with the anti-cathode in its furthest position

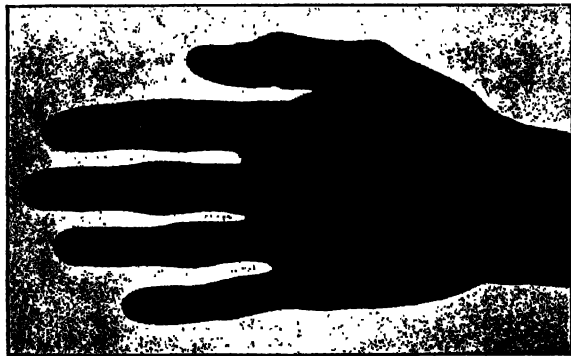


FIG. 16.

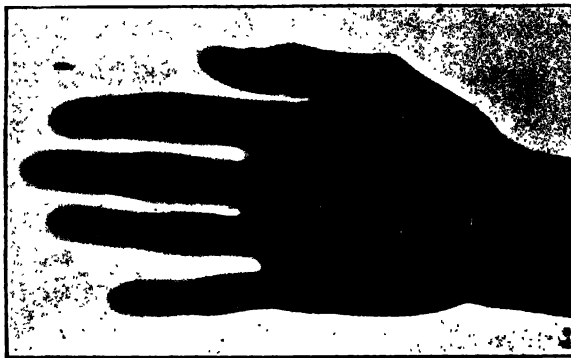


FIG. 17.



FIG. 18.

Photographs showing varying penetration obtained with an adjustable cathode tube.

from the cathode, and moving it gradually towards the latter, it will be observed that at first there is a slight gradual increase in the length of the alternative spark. Then for the next small movement

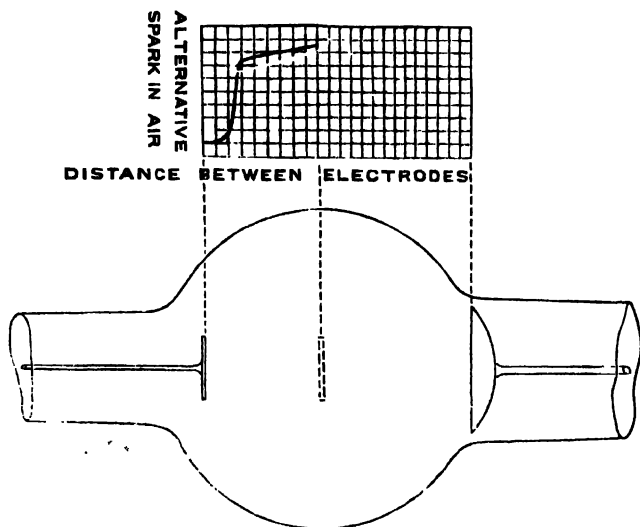


FIG. 19.—Diagram showing how the resistance of a tube is altered by varying the position of the anode.

there is a very sudden increase, and after that again a gradual increase till we get to the point marked in dotted lines, which denotes the limit of travel that the anti-cathode was allowed.

Now let us come to Fig. 20, which represents the effect of moving the cathode in the same tube, the anti-cathode being stationary in the position shown. Here, as will be seen, the less the distance between cathode and anti-cathode the less is the length of the alternative spark.

This distance in this case does not appear, however, to be the determining factor, as it is more than counterbalanced by the more important factor of the position of the cathode relatively to the glass walls of the tube. We have a gradual decrease in the length of the alternative spark as the cathode is moved a little towards the anti-cathode, then a further much more rapid decrease as the cathode emerges from the annex, and a still further slight decrease as it is moved away from the glass walls out into the bulb.

Now as to the effect upon the Röntgen rays, as it has been before remarked, the greater the resistance of the tube and the greater the E.M.F. necessary to cause a discharge to pass, the greater is the

velocity of the atoms that form the cathode rays, and the more penetrative are the Röntgen rays produced. Further, so far as the moving

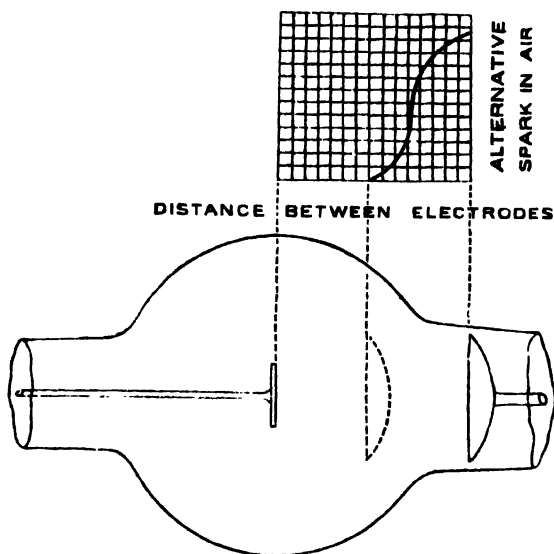


FIG. 20.—Diagram showing how the resistance of a tube is altered by varying the position of the cathode.

cathode is concerned, the supply of atoms appears to be of great importance. If penetrative Röntgen rays are desired the access of atoms to the cathode must be restricted. If only a few atoms can get to the cathode these are projected at great velocity; if there is too ready access the atoms crowd in upon the cathode and the electrical charge of the latter is unable to throw them off with much speed. It is possible to restrict the supply of atoms to the cathode either by bringing the latter back into a recess or annex, as in the tube just shown, or a tube such as is illustrated in Fig. 21, in which both cathode and anti-cathode are fixed, but in which there is a movable conical glass shield which can be brought up from behind the cathode so as to impede the access of the atoms, which, as we have seen, come in round the edges of the cathode, to any desired extent. This tube regulates just as did the adjustable cathode tube, and its efficacy goes a long way to prove that the theory as explained above is substantially correct.

In order to produce sharply defined Röntgen photographs it is of course of the utmost importance that the rays should be given off

from a very small area or point. The sharpness of definition varies considerably with different tubes, and a ready means of judging as to their quality in this respect is very useful. I have here a very pretty arrangement for this purpose which is the idea of Mr. Mackenzie Davidson. It consists simply of a square wooden frame over which are stretched at equal distances a number of parallel wires. There are two sets of wires crossing one another at right angles. By holding this screen near the tube and examining the shadows cast by the wires upon a fluorescent screen at different distances, it is easy to see whether the definition of the tube is good or bad. Here are three Röntgen photographs of the wires, all taken at the same distance but with different tubes. As will be observed, they vary very considerably as regards distinctness, showing that the tubes were very unequal in definition.

Fig. 22 shows a photograph of the wires taken almost in the plane of the anti-cathode, the shadow of which is visible at the right of the picture. As will be observed, the shadows of the wires parallel to the plane of the anti-cathode become less and less distinct the further they are from the latter, while the wires that are at right angles to the anti-cathode plane are exceedingly indistinct. This is of course due to the Röntgen rays being given off from a spot of considerable area in the particular tube with which this photograph was taken, and to the projection of the active area

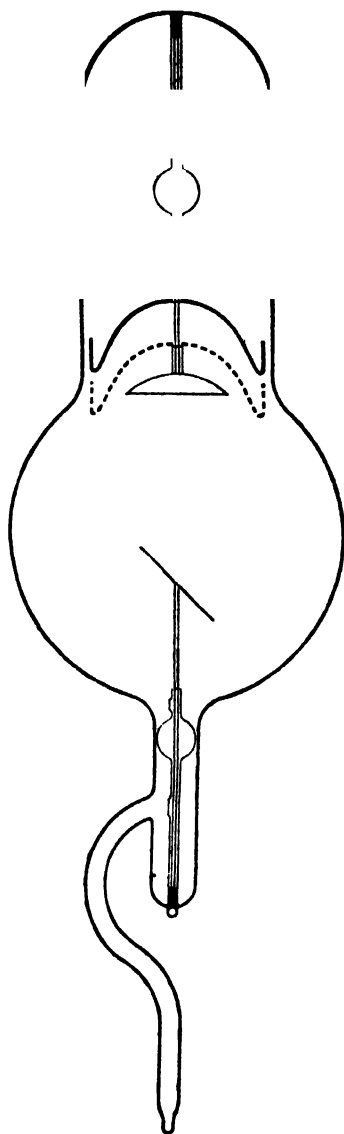


FIG. 21.  
Tube with adjustable glass shield.

becoming more and more of a line when viewed nearer and nearer towards the plane of the anti-cathode.

The best and most accurate way of investigating the area of the anti-cathode from which the Röntgen rays proceed is by means of pin-hole photography. Seeing that the Röntgen rays are not refracted, photography with a lens is of course out of the question, but with a pin-hole very fairly accurate and distinct images can be obtained. It is only necessary to place a sheet of lead, pierced by a pin-hole, near the tube, and then to examine the rays coming through the hole with a fluorescent screen placed some way behind the lead

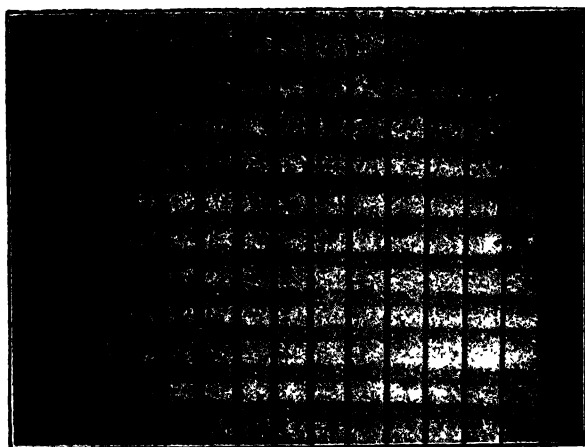


FIG. 22.—Röntgen ray photograph of a wire screen, taken almost in the plane of the anti-cathode, showing astigmatic effect.

sheet, in order to see exactly the size and shape of the active area of the anti-cathode; or instead of the screen a photographic plate may be employed and the effect recorded.

Fig. 23 shows four pin-hole photographs of the anti-cathode taken in this way, giving the effect produced with four different distances between the cathode and anti-cathode. The largest figure is produced with the greatest distance, and *vice versa*. It will be observed that owing to the anti-cathode being placed obliquely to the cathode the figures are all oblique, though somewhat imperfect, conic sections; further, that when the distance between cathode and anti-cathode is great, we have a section of the divergent cone giving a hollow ring with a central spot, just as was visible with the carbon anti-cathode. The ring gets smaller and smaller, and finally disappears as the distance between the electrodes is reduced and the focus approaches the anti-cathode. It will also be noticed that where in the ring portion of the figures the cathode rays strike most normally, that is to say,



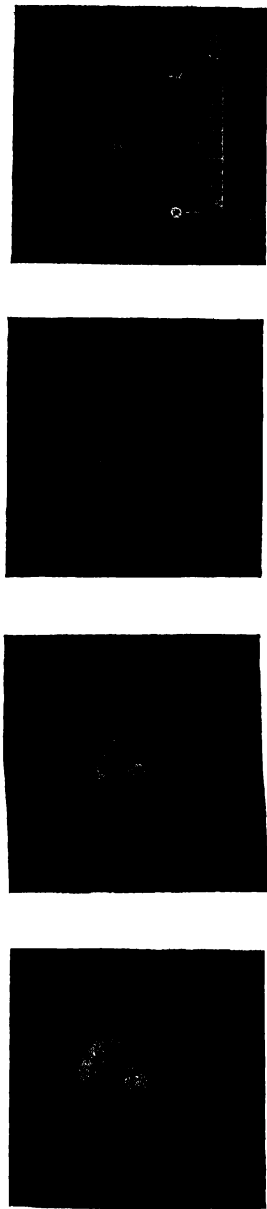


FIG. 23.

Pin-hole Röntgen ray photographs of the active anti-cathode surface for four different distances between cathode and anti-cathode.



FIG. 24.

Similar photographs to the above, but taken almost in the plane of the anti-cathode, across the major and minor axes of the active anti-cathode surface.

at one of the two points of greatest curvature of each ellipse, the Röntgen rays are produced more actively than in the remaining portion, where the cathode rays impinge on the anti-cathode more on the slant. This is still more marked in Fig. 24, which shows what are practically sections through the major and minor axes of one of the images shown in Fig. 23. They were taken similarly to the others, but with the pin-hole and photographic plate almost in the plane of the anti-cathode.

By some it is imagined that because the Röntgen rays are so very penetrating, therefore they are of the nature of an invisible light of great intensity, which though not affecting the human retina acts upon photographic plates very powerfully. This is quite erroneous, and as a matter of fact the photographic effect of Röntgen rays is relatively very feeble. I have investigated this by means of two photographic plates which I have exposed respectively to a very powerfully excited Röntgen ray tube, screened by black paper to remove the visible luminosity, and to the light of a single standard candle. The Röntgen ray tube was employed at a distance of two feet, and the candle at a distance of ten feet, so that according to the law of inverse squares, which holds good for Röntgen rays as for light, the intensities of the two radiations, supposing them to be equal to start with, would be in the proportion of 25 to 1. Each plate was exposed in sections for varying lengths of time, five, ten, fifteen seconds, and so on, each succeeding section being exposed five seconds longer than the preceding one. By sliding the two negatives past one another it is possible to compare them very accurately, and the section exposed to the light of the standard candle for ten seconds is almost exactly of equal density to the section exposed to the Röntgen rays for twenty-five seconds. The photographic power of this particular Röntgen ray tube—and it was a very good one—was therefore less than one-sixtieth of that of one standard candle.

With regard to the true nature of the Röntgen rays there have been many theories. There is the original suggestion of Röntgen himself, that they may possibly consist of longitudinal waves in the ether. Others have thought that they were possibly ether streams or vortices. There is a theory propounded by Tesla and others that they consist of moving material particles, atoms or corpuscles, similar to the cathode rays, which reminds one of Newton's corpuscular theory of light. There is the more generally received doctrine that they are simply exceedingly short transverse ether waves similar in all respects to the waves of light, only so much shorter than the most ultra-violet waves hitherto known that they pass between the molecules of matter, and are consequently neither refracted nor easily absorbed or reflected by any media. Lastly, there is the theory first suggested to the writer early in 1896 by Professor George Forbes, and recently independently enunciated and elaborated by Sir George Stokes, which imagines them to be frequently but irregularly repeated, isolated, and independent disturbances or pulses of the ether, each pulse being similar perhaps to a single wave of light, and consisting

of a single transverse wave or ripple, but the pulses following one another in no regular order, or at any regular frequency as do the trains of vibration of ordinary light.

Then again, there is the question of the mechanism by means of which the Röntgen rays are produced. They are generated by the impact of the cathode rays upon the anti-cathode, and it is now becoming more and more certain that the cathode rays consist of negatively charged atoms travelling at enormous velocity. If we accept this view, there are obviously several methods by which we may imagine the Röntgen rays being generated by the impact of the travelling atoms upon the anti-cathode. Each cathode ray atom carries a negative charge, while the anti-cathode is positively charged, so that when the two come into contact an electrical discharge will take place between them. An electrical oscillation will thus take place in the atom just as in the brass balls of a Hertz oscillator, and transverse electro-magnetic waves will be propagated through the ether in all available directions. As the electro-static capacity of the atom must be exceedingly small, the periodicity of oscillation and the wave frequently will be enormous, while at the same time the oscillation will probably die out with sufficient rapidity to admit of only one or two complete periods. At the same time the greater the difference of potential between atom and anti-cathode at the moment of impact the greater will be the amplitude of oscillation, and the more vigorous and far-reaching the etheric disturbances.

Or we may imagine a more purely mechanical origin for the Röntgen rays. It is believed that the velocity of the cathode rays is enormous, being, as recently measured by J. J. Thomson, over 10,000 kilometres per second, and though Lodge, in his well-known endeavours to detect a movement of the ether by dragging a material body through it, obtained only negative results, of course he could not possibly obtain any velocity at all comparable to this. Assuming that at the velocity of the cathode ray atoms these do appreciably drag the ether with them, there may be some ether effect produced analogous to the atmospheric effect that is noted as the crack of a whip or a clap of the hands, as each atom hits the anti-cathode and rebounds.\*

Or again, it is conceivable that the phenomenon is merely one of heating, and that the cathode ray atoms are by impact with the anti-cathode raised to such an enormous temperature that they give off for a short space of time super-ultra-violet light. Taking a velocity for the atoms of  $10^9$  centimetres per second, as found by J. J. Thomson to be the minimum velocity of the cathode rays, and calculating the temperature to which a nitrogen atom would be raised if, when travelling at this speed, it were instantly brought to rest

\* Since the above was written, the writer's attention has been drawn to Professor J. J. Thomson's paper, "A Theory of the Connection between Cathode and Röntgen Rays," in the 'Philosophical Magazine' for February, in which it is suggested that Röntgen rays consist of very thin and intense electro-magnetic pulses produced in the ether by the sudden stoppage by the anti-cathode of the electrified particles of the cathode rays.

and the whole of its energy converted into heat in the atom itself, we have according to the formula

$$\text{in which} \quad T = \frac{V^2}{2JS},$$

$T$  = the rise in temperature in degrees centigrade ;

$V$  = the velocity in centimetres per second ;

$J$  = joules equivalent ;

$S$  = the specific heat of nitrogen, we have the result that the rise in temperature is no less than the stupendous figure of approximately 50,000,000,000 degrees centigrade.

This is upon the probably erroneous assumption that the specific heat remains constant ; but allowing for this, and even allowing for the merest fraction of the energy being converted into heat in the atom itself, there is obviously an ample margin to admit of a temperature being actually obtained enormously transcending the electric arc or anything of which man has any knowledge. Perhaps it may be objected that it is only when we come to deal with aggregations of atoms that we can speak of heat, and that a hot atom is a physical absurdity. If, however, we look upon heat as a rhythmic dance of the atoms, perhaps we may also contemplate the possibility of a single atom executing a *pas seul*, and giving pulses to the ether at each of its movements. In any case this difficulty disappears if we imagine the cathode ray particles each to consist of an aggregation of atoms.

The fact that substances of high atomic weight form the most efficient anti-cathodes, lends force to the suggestion that the Röntgen rays are produced in some way by the sudden removal of velocity from the atoms that form the cathode rays, owing to the collision of these latter with the comparatively stationary atoms of which the anti-cathode is composed ; while the effect observed with the pin-hole photographs of the anti-cathode, in which, as has been seen, the cathode rays that strike the anti-cathode most normally are the most effective in producing Röntgen rays, is also in accordance with this view. At the same time, the fact that in Röntgen ray photographs of Birkeland's cathode ray spectrum it is always the least deflected ray that produced the greatest photographic effect, goes to show that the higher the velocity of the cathode ray atoms the more effective these latter are in generating the Röntgen rays.

In conclusion, I must express my great indebtedness to the very able assistance of Mr. J. C. M. Stanton and Mr. H. L. Tyson Wolff. The latter has blown nearly all the tubes that I have been able to show this evening, while the aid of the former has also been of great value in a class of experimenting that requires much time and labour.

More than two years have now elapsed since the date of Röntgen's discovery, and nearly twenty years since the commencement of the researches of Crookes. Here, as always, we find that "Art is long, opportunity fleeting, experiment uncertain, judgment difficult." Thus wrote the Greek Hippocrates some twenty-three centuries ago, and time has not impaired the truth of the ancient aphorism.

[A. A. C. S.]

Friday, February 4, 1898.

SIR WILLIAM CROOKES, F.R.S. Vice-President, in the Chair.

ALAN A. CAMPBELL SWINTON, Esq. *M.R.I.*

*Some New Studies in Cathode and Röntgen Radiations.*

THE researches of Crookes, Lenard and Röntgen have given to man a new eye. They have perhaps also given to nature a new light. They have certainly given to science more than one new problem.

This small glass bulb which I hold in my hand, which, being exhausted to a high vacuum, contains, besides its two aluminium electrodes, only a few billions of molecules of residual gas, may appear but a simple piece of apparatus. Could it, however, only be induced while under the stimulus of an electric discharge to reveal in their entirety the secrets that it contains, we should know much at present utterly unknown, not only as regards the nature of electrical action, but also in reference to the fundamental constitution of matter, and the true mechanism of energy. It is, in fact, for the reason that within the Crookes radiant-matter tube, where molecules are separated by comparatively long distances, it is possible to deal not as in everyday life with aggregates of matter, but even individually, perhaps, with single molecules and atoms floating apart in space, that so much attention is at present being devoted to this particular branch of physics.

Every one is now acquainted with what has become the quite ordinary phenomenon of the cathode rays. I turn on the induction coil spark to this highly exhausted tube, and from the aluminium plate that forms the negative electrode or cathode, there proceeds, as you see, some kind of ray that excites a green luminescence in the glass upon which it falls. I interpose in the path of these cathode rays a screen, made of aluminium in the form of a cross, and the latter casts a sharp shadow on the glass. I have here a coil of wire, through which an electric current is passing, and as I slowly move the coil so as to encircle the tube, and consequently gradually increase the strength of the magnetic field within the tube, it will be observed that the shadow of the cross rotates, becoming at the same time smaller. Here we obviously have a deflection of the cathode rays from their rectilinear path, the action of a magnetic field of this description being to concentrate the rays and also to give them a twist, the direction of which depends upon the direction in which the current is sent through the coil of wire.

colours that we can use, for evidently simplicity is a great desideratum, and the number agreed upon must settle the number of separate photographs required.

This brings us to the question of how we see colour, and how many sensations of colour we have. I am not going into the debatable ground of rival colour-vision theories, but I am going to adopt for to-night that one which will answer every practical purpose, and that is the Young theory, in which it is held, and held correctly, that a red, a green, and a blue sensation are alone needful to produce the sensation of any other hue by admixture one with another. The fundamental colour sensations are not necessarily identical with any particular colour, but as a matter of fact, at all events one of these sensations is to be found excited singly in the spectrum, viz. that which is excited by the extreme red. The extreme violet seems to be a compound of two sensations, one a deep blue and the other red, so that the pure blue and also the green sensations can never be singly stimulated in the normal eye. The diagram shows these sensations as curves representing the stimulations by the spectrum colours of the seeing apparatus in the retina (Fig. 1). The scales on each curve are so adapted that when the ordinates of the sensation curves are equal we get white. To get a yellow, the red sensations and green sensations are equally stimulated, for there the curves cut. It will be seen that the purest green sensation is largely mixed with white, for at one point, where the red and blue curves cut, the green curve is above them. At that point, then, the red and

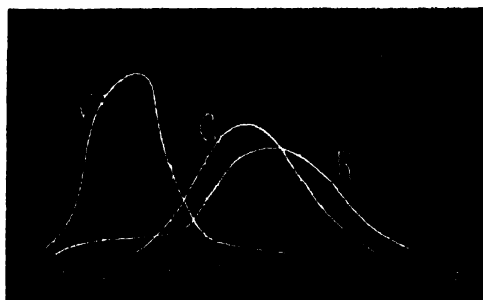


FIG. 1.

blue, and a certain portion of green, go to form white, and the balance is green, so here the pure green sensation is diluted with white. At any other point it is mixed with some other sensation, either red or blue, and also up to certain points with white. Of course, if we could get three colours which only stimulated respectively the three fundamental sensations, we should take three appropriate photographs of the spectrum and illuminate them with those three colours.

But the amount of white which is in the purest green sensation, renders it desirable to choose a green which has less white inherent in it, to prevent the mixture being pale.

In 1861, Clerk Maxwell gave a lecture in this theatre, in which the method of producing photographs in the colours of nature by means of illuminating three photographic pictures, and combining the images together, was foreshadowed, and it is to this, and to his

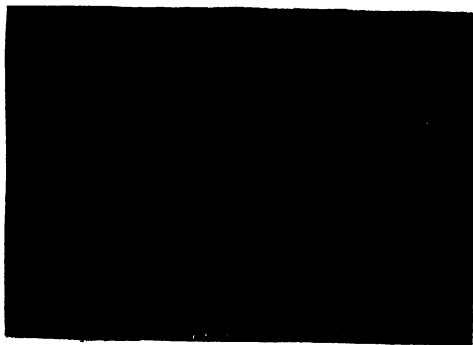
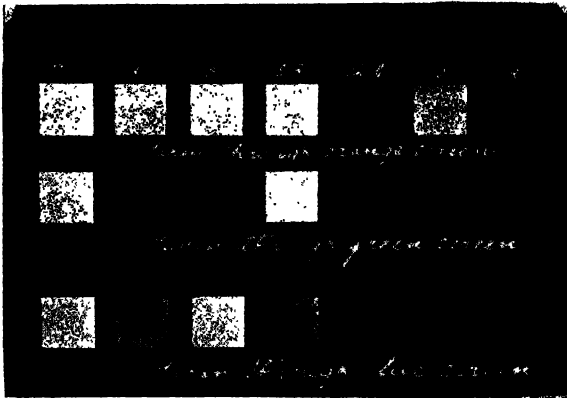


FIG. 2.—Maxwell's Curves of Colour Sensations.

original work on the mixture of colours; that we must turn. By means of what he called his colour-box, he could mix any three colours of the spectrum together, and, for reasons which appeared adequate at the time, he took a bright red, a bright green, and a bright blue of the spectrum as best representing the sensations. He referred all other colours of the spectrum to these, and expressed them as mixtures of the three. The diagram that he made is given (Fig. 2). The heights of the different curves he obtained by measuring the width of the three slits through which any three chosen colours came, and making such widths the ordinates. The standard red he chose was a red containing a little green; the standard green near E is nearly free from white, but a glance at the diagram (Fig. 1) will show it is mixed with a certain amount of red; Maxwell's blue contained a certain quantity of green. This is merely history, but it may be remarked that where we are dealing with colours, and not sensations, the colours he chose are probably nearly the best for the purpose we have in view. I have reduced the Maxwell curves so as to represent luminosity as well as colour, and you will see that they all fit into the spectrum curve, and that the great mass of brightness is due to the green and red. Of blue there is but very little. These curves should be kept well in your mind.

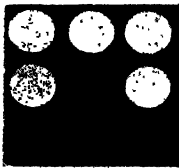
We need not trouble you much about colour mixtures. I have an apparatus here which allows us to mix any colours together

FIG. 3.

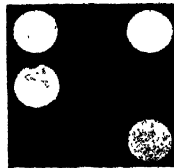


White. Violet. Blue. Peacock Chromium Orange. Red.  
Green. Green.

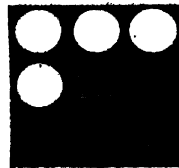
FIG 4.



Red Image.



Green Image.



Blue Image.



Fig. 5.

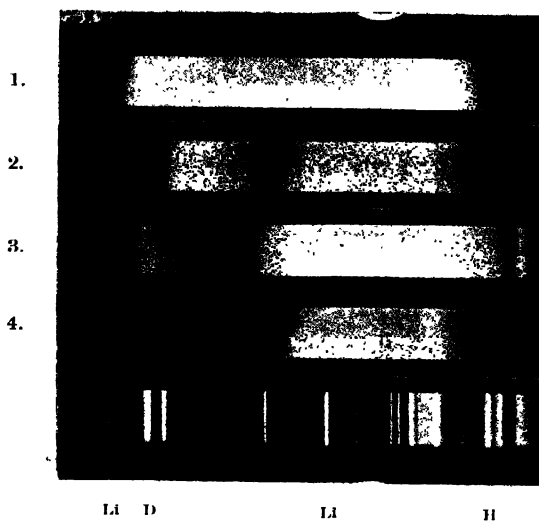
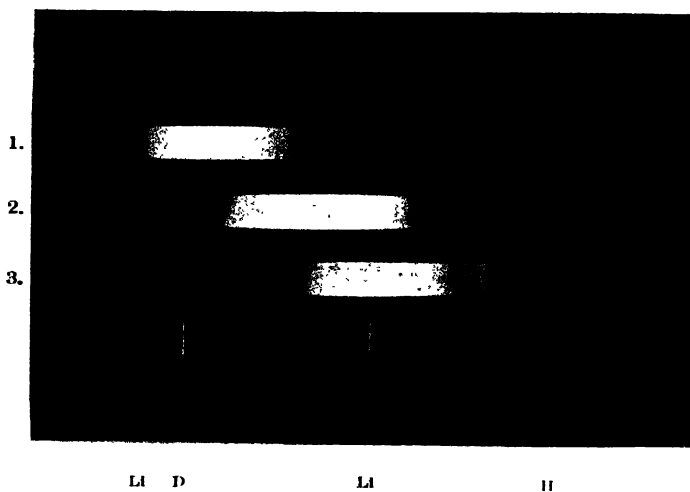


Fig. 6.



In the small spectrum we can place three slits and make a patch of white light. By altering the width of one or two of the slits we can form colours of any hue. [*White was here matched, and three other colours made, and again white.*] Instead of light being diminished by alteration of the width of the slit, we can cut off varying quantities from each ray and allow them to impress the retina for different times, the persistence of vision blending the impressions together. In fact, by an artifice of the kind I have here, which consists of a long band of paper punctured along the three lines of the slits with holes of different sizes, and passing the strip in front of the slits, we can play a regular tune in colour. [*Shown.*]

But we can get these same tunes of colour, though not quite so pure (i.e. unmixed with white) if we use considerable parts of the spectrum. The slits are withdrawn, and all those parts of the spectrum which can come through the holes are mixed together and the colours are reproduced, but not in quite such purity as before.

There is another method of altering the intensity of the rays, and that is by placing in front of the slits photographic deposits of different opacities, and you see that we have, as before, different colours produced. The diagram (Fig. 3) shows a print of the deposits employed. The three rows represent the transparencies of white, violet, blue, peacock blue, dark green, orange and red, taken through an orange, a green, and a blue screen respectively. The three left-hand squares in the transparency covered the three slits, and white was formed on the screen. The next three squares gave a violet, the next three a blue, and so on. This is the foundation of colour photography. Having learnt that the colours mixed together need not be single rays of the spectrum, but may occupy adjacent parts on each side of the single ray and still produce approximately the same results, we can go a step further, as it shows that we may use the light coming through media such as coloured glasses instead of pure spectrum colours.

An interesting experiment is to imitate the spectrum by means of a red, a blue and a green glass. A slit is placed in the lantern, and an image of it thrown on the screen. We have a disc formed of these three glasses, each being shaded by an appropriate mask, to imitate the extent of each sensation in the spectrum. This disc rotates in front of the slit. The varying combinations give a large range of colour, and we have a tolerable representation of the spectrum produced.

I think now we are in a position to realise what is required in order to reproduce by photography the spectrum with all its colours. We must get three photographic negatives, each one of which will take in only so much of the spectrum as is represented by the colour sensations as shown in the diagram, and secure that the brilliancy of the light coming through the transparencies or positives taken from the negatives at each part shall be represented by the heights of the curves, the maximum height in the positive being represented in each

case by bare glass. Behind the "red" photograph we place a red medium, such as red glass, which occupies but a small part of the spectrum and is equivalent to the red sensation, and behind the green photograph a green medium, also taking in but a small part of the spectrum, and behind the blue photograph a blue medium, and if the luminosity of the mixed light coming through the red, the green, and the blue when unshaded by the positives forms white, we shall have a representation of the spectrum.

Suppose that we were going to reproduce the image of the electric light carbons by combining three distinct photographs together backed by proper media, and that we wished to know what each transparency would look like when illuminated with its proper colour, we can show this in a fairly simple manner. Close in front of the slit of the spectroscope is a lens of such a focus that a sharp image of the carbon points is thrown on the surface of the prism. The prism analyses the colours, and a lens in front of the spectrum collects the coloured rays again and gives us an image on the screen of the carbon points. Placing three slits in the spectrum, we alter their width until the image again appears white at the brightest part. We may substitute three lenses of equal foci for the single lens, and we have three images side by side, which, as just seen when combined together, will give the white image of the crater and the redder image of those parts where the heat is less intense. We can vary this experiment. If we place against the prism a small square made up of circular glasses of different colours, we have the image of the glasses on the screen when the whole spectrum is used. With the slits inserted as before, we also get white light and the colours of the glasses (Fig. 4). The three lenses, also placed before the slits, give the separate images such as we wish to obtain by photographic means.

But how about securing these photographs? Can we find three different photographic plates which will be exactly sensitive to the required parts of the spectrum, excluding all other parts?

It will be seen that the parts overlap (see Fig. 1). Thus the green and red curves overlap, as do also the green and the blue. It may at once be stated that there are no such different kinds of plates to be found. But if we can find one plate which is sensitive to the whole spectrum, we can, by using absorbing media, cut off those portions which are required. Now the ordinary plate, with short exposure, is not sensitive much beyond the blue (see No. 4, Fig. 5), but if we give it a slightly longer exposure it will be found sensitive to the green and yellow as well, and, with a still further exposure, to the extreme red; so that we can use an ordinary plate for the purpose, as it is sensitive, but in vastly different degrees, to the whole spectrum, but we have to cut off all the parts we do not want.

In the spectrum of the light transmitted by an orange glass in the spectrum, we see that the red, yellow and green alone penetrate, and this is the region of the spectrum that the red sensation curve occupies. A blue-green glass cuts off most of the red and the violet, and

this gives the part occupied by the green sensation curve; and so with the blue. Evidently, then, by using the orange, blue-green and blue media for the three photographs of the spectrum, we shall secure three negatives representing, with some degree of exactness, the sensation curves, though the exposures given to each one will be very different. The red will require nearly one hundred times more exposure than the blue, and the green an intermediate exposure. On the screen we have the negatives obtained, and also the positives (Fig. 6). No. 1 was taken through the orange, No. 2 through the green, and No. 3 through the blue screen. The superposed images of these three positives, if backed by red, green and blue light, will give us the spectrum. [*Mr. Ives showed the projection on screen.*] The picture is fairly perfect, and exemplifies what can be done with an ordinary plate.

What I wish to impress upon you is that the screens used for the taking of the three different negatives must each allow a large part of the spectrum to pass, whereas the colour screens used to illuminate the three positives, where the images are superposed, will be more efficient the smaller the part of the spectrum that is used, for if large parts are used the colours will be tinged with white. This is a most important point in three-colour photography.

We have modifications of plates which allow shorter exposures to be given to the green and the red. Cadott's spectrum plate (see No. 1, Fig. 5), for instance, can be utilised for giving equal exposures through a blue, a green and a red medium, when the white light is first toned down to a pale yellow, which, however, still contains all the colours of the spectrum.

Then there are others, such as Lumiere's (see Nos. 2 and 3, Fig. 5), which are sensitive to the green and yellow and red, as well as to the blue, but which exhibit gaps in sensitiveness in the length of the spectrum. These plates can be utilised for photographing colours in nature, though they must fail for photographing the spectrum. But to atone for the gaps, the absorbing media used have to be modified to effect a compromise as it were. Mr. Ives, who is the inventor of the Photochromoscope, and who is present this evening to show some of his wonderful results, has kindly lent me a slide showing the screens with which to take the three negatives with Lumiere's pan-chromatic plates.

By modifying the screens, any plate which is sensitive to the yellow and orange may be utilised, even though it is not at all, or only very feebly, sensitive to the red. For be it remembered that the colours in nature are not pure spectrum colours. A red, for instance, such as this glass, contains an appreciable amount of yellow in it, and the yellow will impress the plate sufficiently to answer the purpose of obtaining the requisite density to represent the red. Of course, if there were a red of a spectrum simplicity, it would not impress the plate. Except with the ordinary plate such as I have used, there has to be a series of compromises. Again, it must be

remembered that the negatives obtained have to be converted into positives; and further, that for effective working all three negatives must, in ordinary circumstances, be obtained on one plate, and by one length of exposure. Mr. Ives has worked this out with a wonderful degree of exactitude, and his camera can be examined in the Library after the lecture to show the manner in which he has accomplished it. He has aimed at getting a perfectly graduated negative with each colour screen, and in the positives from them there are absolutely transparent parts, thus securing the maximum brilliancy.

These positives are backed by colour screens chosen to imitate the three colours used by Clerk Maxwell in his colour mixture equations.

Now, having explained the principles of the three-colour photography, I will get Mr. Ives to throw three or four of his pictures on the screen, and I have to thank him for his ready acquiescence in responding to my request for his help to-night. It is a pleasure to acknowledge that Mr. Ives has been the pioneer in this colour photography, working on exact principles, which he has applied to practical purposes.

In connection with the same subject we have the more recent process due to Professor Joly, of Dublin. Instead of taking three negatives and from them three transparencies, he combines the three in one. To take his negatives he observes the same general principle as that already enunciated, for he places in contact with his sensitive plate a screen consisting of a series of orange, green and blue lines ruled on white glass and touching one another; each line is  $\frac{1}{36}$  of an inch in width. Every third line is a colour screen in orange, the next line and third from it a green, and the remaining ones blue. To tone down the excess of blue in daylight, the lens is covered with a pale yellow screen. The one negative is therefore a mixture of three colour negatives. A transparency is taken in the usual way, and by placing in contact with it a screen ruled in red, green and blue, the red lines occupying the position of the orange line in the taking screen, the green the green, and the blue the blue, we have a representation in colour of the original object. [The taking screen, the viewing screen, and a negative and a positive were shown, as also a selection of finished pictures taken by Professor Joly.]

Suppose we take one set of Ives' negatives and make duplicate prints from them in bichromated gelatine, we should get, on development, transparent gelatine of different thicknesses. Where the light had most acted the film would be thickest, and where no light had acted the gelatine would be practically absent, and the intermediate intensities of light acting would give intermediate thicknesses of gelatine. We may dye one set of gelatine prints with a transparent red, a transparent green and a transparent blue, to imitate the viewing screens, and if these were superposed we should find a very different result to that obtained by triple projection. What ought to be black

would be white, and what ought to be white would be black, and the colours shown would be complementary. A yellow *by projection* we know is caused by a full mixture of red and green light, but by superposition the red would cut off all the blue-green light, and the green all the purple light, and the image would be nondescript, and so with other colours. If we dyed the second set of gelatine negatives with the complementary colours a very different state of things would be found. Taking the yellow, for example, which in the "red" and "green" negatives would be shown by great opacity and in the blue by total transparency, the part of the print in the "red" negative would be represented by very feeble sea-green, and that in the green by very feeble purple, whilst in the blue negative it would be represented by full yellow. From the first two the only light penetrating would be the blue, and the only colour reaching the eye after passing through the third gelatine transparency would be the yellow, and so for other colours. Hence, for superposed pictures, either for the lantern or for prints, the complementary colours to those of the viewing screen should be used. This is the foundation of most of the three-colour printing processes extant.

We have three such prints in the three colours, lent me by Messrs. Waterlow & Sons, and here they are superposed to make the final coloured print. This triple printing can be done either by lithography or by printing in colour from gelatine films.

I have endeavoured, by a brief sketch, to show you the principles on which photography in colour has been based—principles which are truly scientific—and which my friend, Mr. Ives, has adopted in all his work. The rule-of-thumb man, who works according to his own sweet will, is a man to whom a certain amount of success will be given, but it is to him who works on the true principles of science that the highest success must accrue. I have endeavoured to show you that Young's theory of Colour Vision, though a theory, is yet of supreme use in this particular branch of industry. I have purposely omitted to mention many of the glaring mistakes which have been made by the rule-of-thumb man, both at home and abroad, in regard to it.

[W. DE W. A.]

Friday, March 4, 1898.

SIR WILLIAM CROOKES, F.R.S. Vice-President, in the Chair.

PROFESSOR T. E. THORPE, LL.D. F.R.S. M.R.I.

*Some Recent Results of Physico-Chemical Inquiry.*

THE lecturer gave an account of the main results of an investigation on the relations between the viscosity (internal friction) of liquids and their chemical nature which had occupied the late Mr. J. W. Rodger and himself during several years. He pointed out, in the first place, that the many attempts which had been made since Hermann Kopp directed attention to the connection which exists between the molecular weights of substances and their densities, to establish similar relationships between the magnitudes of other physical constants and chemical composition, had rendered it highly probable that all physical constants are to be regarded as functions of the chemical nature of molecules, and that the variations in their magnitude observed in passing from substance to substance are to be attributed to changes in chemical composition. As yet, however, all endeavours to connect the chemical nature of liquids with their viscosity have been only partially successful, although it is obvious from the work of Graham, Rollstab, Pribram and Handl, and Gartenmeister, that such a connection ought to be discoverable.

Thus it was known that an increment of  $\text{CH}_2$  in a homologous series is in general accompanied by an increase in viscosity, and that the increase is greater when the increment of  $\text{CH}_2$  takes place in an alcohol radicle than when it takes place in an acid radicle. Metameric bodies have, in general, different viscosity values, and these are nearer together the nearer the boiling points of the liquids. Substances containing double-linked carbon are more viscous than those of equal molecular weight containing single-linked carbon. The substitution in a molecule of Cl, Br, I and  $\text{NO}_2$  for H in all cases increases the viscosity of the substance. This increase is smallest on the introduction of Cl, and increases on the introduction of Br, I, and  $\text{NO}_2$  and in the order given. The absolute amount of the increase depends not only upon the nature of the substituting radicle but also upon its position in the molecule. Of two isomeric esters that possesses the greater viscosity which contains the higher alcoholic radicle. The ester containing the normal radicle has always a greater viscosity than the iso-compound, and this obtains no matter

whether the isomerism is in the alcohol or the acid radicle. The normal aldehydes have invariably a greater viscosity than the isocompounds, whilst the alcohols have a greater viscosity than the corresponding aldehydes and ketones. The introduction of the hydroxyl group into the molecule greatly increases the viscosity of the liquid. This is strikingly illustrated by the instances of propyl alcohol, propylene glycol and glycerin. Indeed the high viscosity of solutions of carbohydrates, e.g. the sugars, gums, &c., is probably dependent on the relatively numerous hydroxyl groups in the molecule. The manner in which the hydroxyl group is combined seems, however, to have considerable influence on the viscosity. Thus in the cases of the isomeric substances, benzyl alcohol and metacresol, it is found that in the first-named substance, in which the hydroxyl group occurs in the side chain, the viscosity is very much less than that of the second, in which the hydroxyl group is attached to a carbon atom in the benzene ring.

Whilst the broad fact of a connection between the viscosity of a liquid and the chemical nature of its molecules is established, it cannot be said that the numerical results hitherto obtained afford any accurate means of determining the quantitative character of this connection. This is owing partly to the imperfection of observational methods, and partly to the uncertainty of the basis of comparison. It seems futile to expect that any definite stoichiometric relations should become evident by comparing observations taken at one and the same temperature. Hitherto few attempts have been made to ascertain the influence of temperature upon viscosity, and hence the law of the variation is unknown. It seemed therefore, obvious, that in order to investigate the subject with reasonable hope of discovering stoichiometric relations, one essential point was to ascertain more precisely the influence of temperature on viscosity, and then to compare the results under conditions which have been found to be suitable in similar investigations in chemical physics. Unfortunately, the accurate determination of absolute coefficients of viscosity is beset with difficulties, both in the theory and practice of the methods which can be employed. Moreover, it is quite possible that even if accurate values of the coefficients of viscosity were obtained, their relationships to chemical composition might not be simple. Viscosity is, no doubt, the nett result of at least two distinct causes. When a liquid flows, during the actual collision or contact of its molecules a true friction-like force is called into play which opposes the movement, whilst at the same time molecular attractions exercise a resistance to the forces which tend to move one molecule past another.

After indicating the meaning of viscosity and the principles involved in measuring it, the lecturer proceeded to point out how the coefficient of viscosity may be defined. It is the force which is necessary to maintain the movement of a layer of unit area past another of the same area with a velocity numerically equal to the distance between the layers when the space between them is con-



tinuously filled with the viscous substance. Ho then described the different modes of measuring viscosity, and explained the general principle of the method and the features of the particular apparatus employed in the investigation made by Mr. Rodger and himself. The principle was that of Poiseuille, and consisted in observing the time required for a definite volume of liquid under a definite pressure to pass through a capillary tube of known size, the temperature being known and kept constant during the interval. The actual apparatus, however, differed in many important features from any previously designed for the same purpose, and admitted of the determination, in absolute measure, of the coefficient for a temperature range from  $0^{\circ}$  up to the ordinary boiling point of the liquid. In most of the instruments used by previous observers, the liquid, after passing through the capillary, was allowed to escape, and hence the apparatus had to be recharged before another observation could be made. In the newer form, the time spent in recharging was saved, by arranging that in all the observations on any one liquid the same sample could be used repeatedly; and further economy in time was obtained by arranging that observations could be taken while the liquid was flowing in either direction through the capillary tube, and that while an observation was in progress and liquid was leaving one portion of the instrument, it was entering another portion and getting into position for a fresh observation. It was also desirable to avoid the use of corks or caoutchouc in such parts as would be in contact with the liquid, and it was therefore necessary that the instrument should be made entirely of glass.

The form of apparatus designed to meet these requirements is shown in Fig. 1; it may be termed a glischrometer. It consists of two upright limbs L and R (left and right), connected near their lower ends by a cross piece. Within the cross piece is the capillary tube O P, the bore of which is about .008 centimetres radius, and the thickness of the wall about 2 millimetres, the internal radius of the cross piece being a millimetre or so greater than the external radius of the capillary. At the zone R, R', the walls of the cross piece are constricted and made continuous with those of the capillary: the latter is thus gripped at its middle portion and held axially within the cross piece. Care is of course taken that the bore of the capillary is in no wise disturbed during the process of sealing.

On one side of each limb of the instrument three fine horizontal

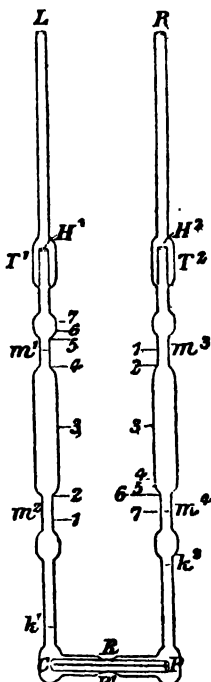


FIG. 1.

lines were etched,  $m^1, m^2, k^1$ , on the left limb;  $m^3, m^4, k^2$ , on the right limb. The volumes of the limbs between  $m^1$  and  $m^2$  and between  $m^3$  and  $m^4$  were carefully determined; these represent the volumes of liquid which flow through the capillary. The time taken by the level of the liquid to pass from the upper to the lower of either of these pairs of marks is the time observed in the experiments. The limb is constricted in the vicinity of the marks, in order to give sharpness in noting the coincidence of the meniscus with the mark. The shape of the limb between the marks was made cylindrical rather than spherical, in order that the contained liquid might the more readily acquire the temperature of the bath in which the glischrometer was placed during an observation.

It will be seen from the figure that the upper ends of the limbs  $H^1, H^2$  terminate within the glass traps  $T^1, T^2$ . These traps admit of slight adjustments of the volumes of liquid contained in the limbs, and their use is connected with that of the marks  $k^1$  and  $k^2$ . During an experiment the levels of liquid in the two limbs are continually altering. The object of these marks and traps is to ensure that at the beginning of any observation in a particular limb the effective head of the liquid contained in the glischrometer shall be constant and shall be known. Let us suppose that an observation is to be made in the right limb; the liquid level in the left limb is just brought into coincidence with the mark  $k^1$ , when any excess of liquid will flow over into the trap  $T^2$ ; hence the effective head of liquid extends from  $H^2$  to  $k^1$ , and is thus known. A similar proceeding is carried out for the left limb observations, using the mark  $k^2$  and trap  $T^1$ . The marks  $k^1$  and  $k^2$  are placed by trial in such positions that the volume from  $k^1$  to  $H^2$  is almost equal to, but slightly greater than, that from  $k^2$  to  $H^1$ . The volumes  $k^1 H^2$  and  $k^2 H^1$  are the working volumes of liquid used in the observations.

The general arrangement of the whole apparatus is shown in Fig. 2. A bath B, which for observations at temperatures below  $100^\circ$  contains water, and for higher temperatures glycerin, is supported on an iron stand which is placed on a table in front of a window.\* The bath is divided into two compartments. The inner compartment is provided back and front with plate glass walls; the rest of the bath is made of brass. The outer compartment bounds the inner at the sides and underneath, and is fitted with a tap for adjusting the quantity of liquid which it contains. The brass framework carrying the glischrometer, and thermometer T, can be lowered into vertical slots in the lateral walls of the inner compartment; when thus situated the glischrometer occupies a central position in the bath. The walls of both compartments are provided with guides, along which move stirrers consisting of brass plates pierced with holes, which are attached to suitable rods and cross pieces, and are worked by a small water-motor W M,

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\* In practice two baths were used, one containing water, the other glycerin.

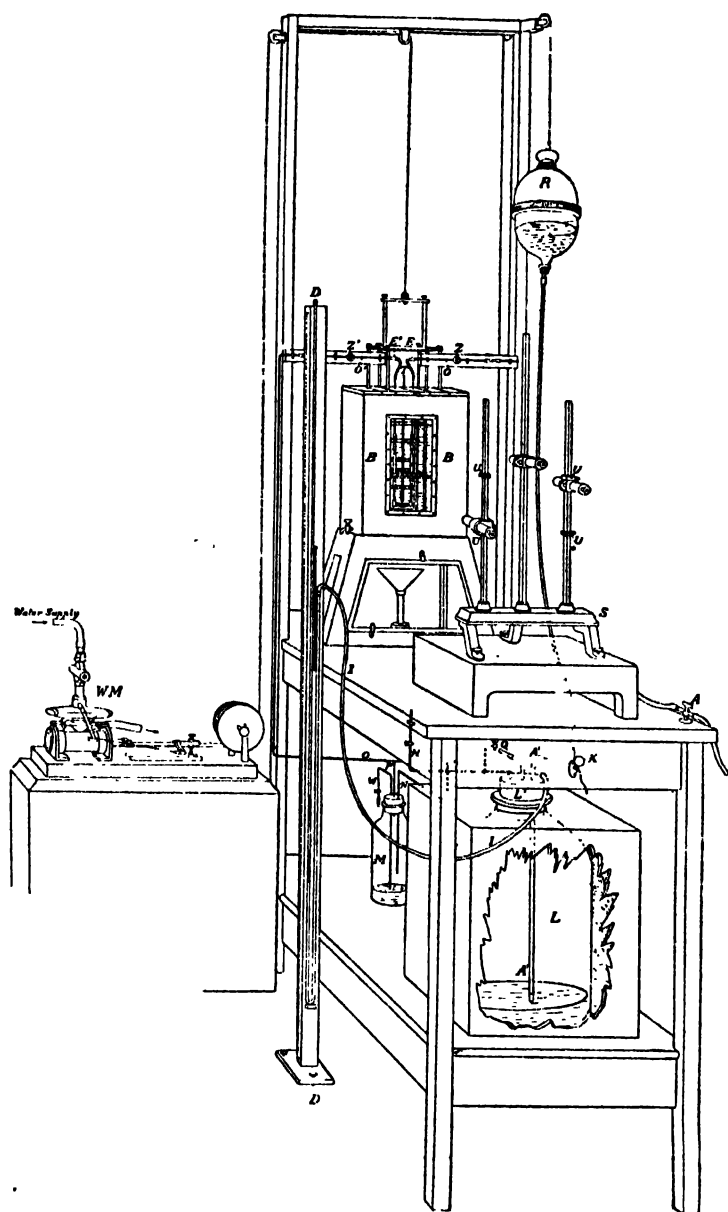


FIG. 2.

The rubber tube E connects the right limb of the glischrometer with the glass tube O, in which is inserted the three-way cock Z. In the same way E' connects the left limb of the glischrometer with the tube O' fitted with the three-way cock Z'. At P, O and O' are united by a T piece which leads to the bottle M containing a quantity of sulphuric acid, which can be abstracted or replaced by means of the syphon W. The acid serves to dry air in its passage from the reservoir L to the glischrometer. When hygroscopic liquids are being experimented upon, the exit tubes of the three-way cocks are provided with small tubes filled with calcium chloride to prevent access of atmospheric moisture to the glischrometer. In this way it is insured that dry air only is in contact with the liquid under examination.

By means of the tube N, which extends from within a few millimetres of the surface of the acid in M to a centimetre or so below the cork L', and which is fitted with the cock Q, the air in M may be put into communication with the large air reservoir L. This consists of a glass bottle of about 30 litres capacity, encased in a wooden box, and surrounded with sawdust to prevent excessive fluctuation of temperature. A glass tube A', which reaches to within 5 millimetres, of the bottom of L, is connected, as shown, by india-rubber tubing with the water reservoir R. The air in L is compressed by raising the water reservoir, the height of which can be regulated by a cord leading by a system of pulleys to the stud X, in close proximity to the observer, and to the water manometer D D which indicates the pressure set up in the confined air space. The manometer is connected with the air reservoir by the tube I I, which has a common termination with the tube N.

After describing the method of making a viscosity observation, the lecturer proceeded to indicate how the coefficients of viscosity for the particular temperatures were deduced from the time and pressure of flow, and the constants of the glischrometer.

The coefficient of viscosity  $\eta$  may be found from the expression—

$$\eta = \pi R^4 t p / 8 l v - \rho V / 8 \pi l t,$$

in which R is the radius of the capillary tube and  $l$  its length, and V the volume of the liquid of density  $\rho$  passing through in time  $t$  and under pressure  $p$ . The negative term of the formula gives the measure of the correction for the kinetic energy imparted to the liquid, as deduced by Couette and Finkener.

With a view of tracing the influence of homology, substitution, isomerism, molecular complexity, and, generally speaking, of changes in the composition and constitution of chemical compounds upon viscosity, a scheme of work was drawn up which involved the determination in absolute measure of the viscosity of between 80 and 90 liquids at all temperatures between  $0^\circ$  (except in cases where the liquid solidified at that temperature) and their respective boiling points.

This list is as follows:—

Water .. .. .	H <sub>2</sub> O.
Bromine .. .. .	Br <sub>2</sub> .
Nitrogen peroxide .. .. .	N <sub>2</sub> O <sub>4</sub> .

*Paraffins and Unsaturated Fatty Hydrocarbons.*

Pentane .. .. .	CH <sub>3</sub> .(CH <sub>2</sub> ) <sub>3</sub> .CH <sub>3</sub> .
Isopentane .. .. .	(CH <sub>3</sub> ) <sub>2</sub> CH.CH <sub>2</sub> .CH <sub>3</sub> .
Hexane .. .. .	CH <sub>3</sub> .(CH <sub>2</sub> ) <sub>4</sub> .CH <sub>3</sub> .
Isohexane .. .. .	(CH <sub>3</sub> ) <sub>2</sub> CH.(CH <sub>2</sub> ) <sub>2</sub> .CH <sub>3</sub> .
Heptane .. .. .	CH <sub>3</sub> .(CH <sub>2</sub> ) <sub>5</sub> .CH <sub>3</sub> .
Isoheptane .. .. .	(CH <sub>3</sub> ) <sub>2</sub> CH.(CH <sub>2</sub> ) <sub>3</sub> .CH <sub>3</sub> .
Octane .. .. .	CH <sub>3</sub> .(CH <sub>2</sub> ) <sub>6</sub> .CH <sub>3</sub> .
Trimethyl Ethylene (β-isoamylene)	(CH <sub>3</sub> ) <sub>2</sub> C : CH.CH <sub>3</sub> .
Isoprene (Pentene) .. .. .	C <sub>5</sub> H <sub>8</sub> .
Diallyl (Hexene) .. .. .	CH <sub>2</sub> :CH.(CH <sub>2</sub> ) <sub>2</sub> .CH:CH <sub>2</sub> .

*Iodides.*

Methyl iodide .. .. .	CH <sub>3</sub> I.
Ethyl iodide .. .. .	CH <sub>3</sub> .CH <sub>2</sub> I.
Propyl iodide .. .. .	CH <sub>3</sub> .CH <sub>2</sub> .CH <sub>2</sub> I.
Isopropyl iodide .. .. .	(CH <sub>3</sub> ) <sub>2</sub> CHI.
Isobutyl iodide .. .. .	(CH <sub>3</sub> ) <sub>2</sub> CH.CH <sub>2</sub> I.
Allyl iodide .. .. .	CH <sub>2</sub> :CH.CH <sub>2</sub> I.

*Bromides.*

Ethyl bromide .. .. .	CH <sub>3</sub> .CH <sub>2</sub> Br.
Propyl bromide .. .. .	CH <sub>3</sub> .CH <sub>2</sub> .CH <sub>2</sub> Br.
Isopropyl bromide .. .. .	(CH <sub>3</sub> ) <sub>2</sub> CHBr.
Isobutyl bromide .. .. .	(CH <sub>3</sub> ) <sub>2</sub> CH.CH <sub>2</sub> Br.
Allyl bromide .. .. .	CH <sub>2</sub> :CH.CH <sub>2</sub> Br.
Ethylene bromide .. .. .	CH <sub>2</sub> Br.CH <sub>2</sub> Br.
Propylene bromide .. .. .	CH <sub>3</sub> .CHBr.CH <sub>2</sub> Br.
Isobutylene bromide .. .. .	(CH <sub>3</sub> ) <sub>2</sub> CBr.CH <sub>2</sub> Br.
Acetylene bromide .. .. .	CHBr:CHBr.

*Chlorides.*

Propyl chloride .. .. .	CH <sub>3</sub> .CH <sub>2</sub> .CH <sub>2</sub> Cl.
Isopropyl chloride .. .. .	(CH <sub>3</sub> ) <sub>2</sub> CHCl.
Isobutyl chloride .. .. .	(CH <sub>3</sub> ) <sub>2</sub> CH.CH <sub>2</sub> Cl.
Allyl chloride .. .. .	CH <sub>2</sub> :CH.CH <sub>2</sub> Cl.
Methylene chloride (Dichloromethane) .. .. .	CH <sub>2</sub> Cl <sub>2</sub> .
Ethylene chloride .. .. .	CH <sub>2</sub> Cl.CH <sub>2</sub> Cl.
Ethylidene chloride .. .. .	CH <sub>3</sub> .CHCl <sub>2</sub> .
Chloroform (Trichloromethane) .. .. .	CHCl <sub>3</sub> .
Carbon tetrachloride (Tetrachloromethane) .. .. .	CCl <sub>4</sub> .
Carbon dichloride (Tetrachloroethylene) .. .. .	CCl <sub>2</sub> :CCl <sub>2</sub> .

*Sulphur Compounds.*

Carbon bisulphide .. .. .	CS <sub>2</sub> .
Methyl sulphide .. .. .	(CH <sub>3</sub> ) <sub>2</sub> S.
Ethyl sulphide .. .. .	(CH <sub>3</sub> .CH <sub>2</sub> ) <sub>2</sub> S.
Thiophen .. .. .	CH:CH.S.CH:CH

*Acetaldehyde and Ketones.*

Acetaldehyde .. ..	$\text{CH}_3.\text{COH}.$
Dimethyl ketone .. ..	$\text{CH}_3.\text{CO}.\text{CH}_3.$
Methyl ethyl ketone .. ..	$\text{CH}_3.\text{CH}_2.\text{CO}.\text{CH}_3.$
Diethyl ketone .. ..	$\text{CH}_3.\text{CH}_2.\text{CO}.\text{CH}_2.\text{CH}_3.$
Methyl propyl ketone .. ..	$\text{CH}_3.(\text{CH}_2)_2.\text{CO}.\text{CH}_3.$

*Acids.*

Formic acid .. ..	$\text{H}.\text{COOH}.$
Acetic acid .. ..	$\text{CH}_3.\text{COOH}.$
Propionic acid .. ..	$\text{CH}_3.\text{CH}_2.\text{COOH}.$
Butyric acid .. ..	$\text{CH}_3.(\text{CH}_2)_2.\text{COOH}.$
Isobutyric acid .. ..	$(\text{CH}_3)_2\text{CH}.\text{COOH}.$

*Oxides (Anhydrides).*

Acetic anhydride (Acetyl oxide) ..	$(\text{CH}_3.\text{CO})_2\text{O}.$
Propionic anhydride (Propionyl oxide) .. ..	$(\text{CH}_3.\text{CH}_2.\text{CO})_2\text{O}.$

*Aromatic Hydrocarbons.*

Benzene .. ..	$\text{C}_6\text{H}_6.$
Toluene (Methyl benzene) .. ..	$\text{C}_6\text{H}_5.\text{CH}_3.$
Ethyl benzene .. ..	$\text{C}_6\text{H}_5.\text{C}_2\text{H}_5.$
Ortho-xylene .. ..	$\text{C}_6\text{H}_4(\text{CH}_3)_2(1:2).$
Meta-xylene .. ..	$\text{C}_6\text{H}_4(\text{CH}_3)_2(1:3).$
Para-xylene .. ..	$\text{C}_6\text{H}_4(\text{CH}_3)_2(1:4).$

*Alcohols.*

Methyl alcohol .. ..	$\text{CH}_3\text{OH}.$
Ethyl alcohol .. ..	$\text{CH}_3.\text{CH}_2\text{OH}.$
Propyl alcohol .. ..	$\text{CH}_3.\text{CH}_2.\text{CH}_2\text{OH}.$
Isopropyl alcohol .. ..	$(\text{CH}_3)_2\text{CHOH}.$
Butyl alcohol .. ..	$\text{CH}_3.(\text{CH}_2)_2.\text{CH}_2\text{OH}.$
Isobutyl alcohol .. ..	$(\text{CH}_3)_2\text{CH}.\text{CH}_2\text{OH}.$
Trimethyl carbinol .. ..	$(\text{CH}_3)_3\text{COH}.$
Amyl alcohol (active) .. ..	$\text{CH}_3.\text{CH}_2.\text{CH}(\text{CH}_3).\text{CH}_2\text{OH}.$
Amyl alcohol (inactive) .. ..	$(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}_2\text{OH}.$
Dimethyl ethyl carbinol .. ..	$(\text{CH}_3)_2\text{C}(\text{OH}).\text{CH}_2.\text{CH}_3.$
Allyl alcohol .. ..	$\text{CH}_2:\text{CH}.\text{CH}_2\text{OH}.$

*Esters.*

Methyl formate .. ..	$\text{H}.\text{COOCH}_3.$
Ethyl formate .. ..	$\text{H}.\text{COOCH}_2.\text{CH}_3.$
Propyl formate .. ..	$\text{H}.\text{COOCH}_2.\text{CH}_2.\text{CH}_3.$
Methyl acetate .. ..	$\text{CH}_3.\text{COOCH}_3.$
Ethyl acetate .. ..	$\text{CH}_3.\text{COOCH}_2.\text{CH}_3.$
Propyl acetate .. ..	$\text{CH}_3.\text{COOCH}_2.\text{CH}_2.\text{CH}_3.$
Methyl propionate .. ..	$\text{CH}_3.\text{CH}_2.\text{COOCH}_3.$
Ethyl propionate .. ..	$\text{CH}_3.\text{CH}_2.\text{COOCH}_2.\text{CH}_3.$
Methyl butyrate .. ..	$\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{COOCH}_3.$
Methyl isobutyrate .. ..	$(\text{CH}_3)_2\text{CH}.\text{COOCH}_3.$

*Ethers.*

Ethyl ether	.. ..	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_3$ .
Methyl propyl ether	.. ..	$\text{CH}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ .
Ethyl propyl ether	.. ..	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ .
Dipropyl ether	.. ..	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ .
Methyl isobutyl ether	.. ..	$\text{CH}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2$ .
Ethyl isobutyl ether	.. ..	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2$ .

In speaking of the results of the observations on these substances the lecturer drew special attention to the case of water, more particularly as regards the effect of temperature in altering its viscosity. The following table shows the viscosity of water in absolute measures at temperatures between  $0^\circ$  and  $100^\circ \text{C}$ .

Temperature.	Viscosity.	Temperature.	Viscosity.	Temperature.	Viscosity.
$0^\circ$		$0^\circ$		$0^\circ$	
0	·01778	35	·00720	70	·00106
5	·015095	40	·006535	75	·003755
10	·013025	45	·00597	80	·00356
15	·011335	50	·005475	85	·00335
20	·010015	55	·005055	90	·003155
25	·00821	60	·00468	95	·002985
30	·007975	65	·004355	100	·00283

The results of these observations are graphically represented in Fig. 3, in which viscosity coefficients are ordinates and temperatures are abscissæ.

A special series of observations was made in order to ascertain if, as inferred by Moritz, water had a maximum viscosity in the neighbourhood of  $4^\circ$ , but no indication was given of any anomalous change in the rate of variation between  $0^\circ$  to  $8^\circ$ , and the lecturer pointed out the bearing of this fact upon the supposition that water at low temperature is a solution of ice, richer and richer in ice as it is more and more cooled.

The so-called anomaly of water possessing a point of maximum density remote from its point of congelation, must be connected with its other physical properties, and observation shows this to be the case. Water, like all other liquids, is compressible, but whereas in the case of all other liquids the compressibility increases with the temperature, it is found that water at low temperature is more compressible than at high temperatures. It has also been shown that water is "anomalous" in respect to its behaviour when heated under pressure. The degree to which it expands for a given interval of temperature steadily increases with the pressure, and especially at low temperatures, contrary to what is usually observed. The viscosity of water is also affected by pressure. It has been shown by Warburg and Sachs, and also by Röntgen, that water at ordinary temperatures

becomes more mobile when subjected to pressure: in other words, its viscosity is lowered by pressure. This is a very striking fact, and so far as observation has gone it is without a parallel. Benzene, ether, liquid carbon dioxide, all become more viscous under the

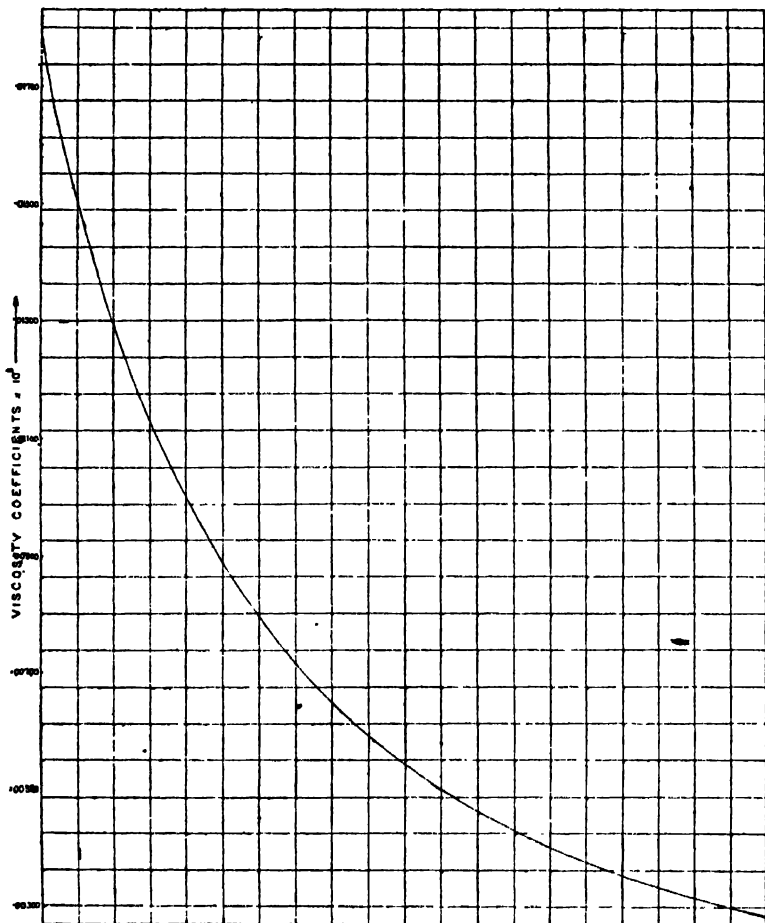


FIG. 3.—Viscosity of Water between 0° and 100°.

influence of great pressure. Now Professor Röntgen has pointed out that these "anomalies" may be explained on the assumption that water at ordinary temperatures is an aggregation of two distinct kinds of molecules, one of which has the properties we associate with



ice. The proportionate amount of these "ice-molecules" depends, under ordinary conditions, upon the temperature. On heating they become fewer and fewer; on cooling they become more numerous. We may regard water at any particular temperature as a saturated solution of such molecules; when cooled below its ordinary solidifying point it is a supersaturated solution of such molecules, and of course behaves under such conditions like any other supersaturated solution.

Now any circumstance which effects the transformation of the ice-molecules into the other kind of molecules should be attended by a contraction of volume. When water is heated from  $0^{\circ}$  upwards, we have two distinct volume changes—expansion of the water as such, and the destruction or transformation of the ice-molecules with consequent diminution of volume. Up to  $4^{\circ}$  the diminution due to the transformation of the ice-molecules is greater than the expansion, and the nett result is contraction. After  $4^{\circ}$  the ice-molecules become fewer and fewer, and the degree of expansion gradually gains upon that of the diminution in volume due to the alteration of the ice-molecules; and thence the degree of contraction becomes less and less, until the nett result is an increase of volume and the water seems to behave like any other liquid on heating. It does not, however, follow that all the so-called ice-molecules will have disappeared, even at above  $8^{\circ}$ , for the two distinct sets of molecules may co-exist, but of course in gradually diminishing ratio as the temperature rises.

It is easy to see how this assumption, which is but an extended form of a very old idea, may serve to explain the "anomalies" above referred to. Take the case of compressibility of water at low temperatures. It is unnecessary to remind a Royal Institution audience that ice, even at low temperatures, may be converted into water by pressure; the classical experiments of Faraday and Tyndall are admirable illustrations of that fact. Now the more ice we thus convert into water the greater the contraction. A given increase of pressure at a low temperature causes a greater contraction than at a higher temperature, because at the lower temperature there are more ice-molecules to be changed. The diminution of volume under compression is like the increase of volume by temperature, made up of two parts, viz. (1) the real compressibility of the water; and (2) the diminution attending the transformation of the ice-molecules. Probably the water-molecules, as such, behave like other molecules—they contract under pressure, and to a gradually smaller extent as the pressure is increased; it is only the effect of the increased pressure in changing the ice-molecules, with consequent diminution of volume, that makes the *apparent* compressibility greater, and thus gives rise to the "anomaly." It should follow, therefore, that at some point of temperature above the freezing point of water there should be a minimum point of compressibility, just as there is a minimum volume. Experiment shows that such a minimum point exists at about  $50^{\circ}$ .

The fact, discovered by Amagat, that water under great pressure is more expansible by heat than at ordinary pressure, may also be equally well explained on this hypothesis. Increasing temperature, as we have seen, works in two directions on the volume of water—but as yet nothing is exactly known of the effect of pressure upon the volume-change per degree of temperature of an aggregate consisting solely of one kind of water-molecules; but the probability is that such an aggregate of molecules would behave like a gas. The anomaly found by Amagat gradually disappears as the pressure is increased. This finds its explanation in the fact that with gradually increasing pressure the number of ice-molecules becomes less. Amagat also found that the anomaly became less marked as the temperature was increased; this also is explained by the circumstance that as the temperature increases the number of the ice-molecules diminishes.

The same hypothesis explains the fact that under pressure the temperature of the point of maximum density becomes lower, and it also affords a reason for the circumstance that the freezing point of water becomes lowered by pressure.

It has been observed that water at low temperatures becomes colder when subjected to pressure, which may be explained by the fact that in order to convert ice-molecules into molecules of the second kind, heat is required, which can only be furnished by the compressed liquid.

As regards the influence of pressure on viscosity, we have only to assume, as analogy indicates, that the greater the number of ice-molecules in solution the more viscous becomes the liquid. If we add soluble matter to water, its viscosity increases. Sea water is more viscous than pure water, and the greater the amount of salt in solution the greater becomes the viscosity. If by pressure we diminish, for any particular temperature, the number of ice-molecules in solution, it must follow that we diminish the viscosity, which is what is observed.

Now, in the light of Professor Röntgen's explanation, the behaviour of water is no longer "anomalous." Its normal properties are exactly similar to those of any other liquid. The so-called anomalies are simply due to the circumstance that the "solid" form of water is specifically lighter than the liquid form. The peculiar form of the curve showing the relation between viscosity and temperature in the case of water at low temperatures, arises from the progressive and rapid increase of the number of the ice-molecules. In this special particular water is not peculiar. Studies on surface energy, on vapour pressures and densities, and on optical characters, have shown that this hypothesis of molecular complexes is well founded, and it is remarkable that many liquids, especially hydroxyl combinations, in which there is reason to assume the existence of such complexes, also exhibit curves of viscosity very similar in character to that shown by water.

The mathematical expression of the relation of the viscosity of

liquids to temperature has engaged the attention of many physicists from the time of Poiseuille, but, on the whole, no empirical formula reproduces the observed values better than that of Slotte, which may be written in the shape—

$$\eta = C / (a + t)^n.$$

In order to determine the value of the constants two values of  $\eta$ , viz.,  $\eta_1$  and  $\eta_3$ , are chosen, which correspond respectively with the temperatures  $t_1$  and  $t_3$ ; a third value of  $\eta$ , viz.  $\eta_2$ , is then found from the equation  $\eta_2 = \sqrt{\eta_1 \eta_3}$ , and the temperature  $t_2$  corresponding with this value  $\eta_2$  is found graphically, and  $a$  and  $n$  are deduced from the equation—

$$a = \frac{t_2^2 - t_1 t_3}{t_1 + t_3 - 2t_2} \quad n = \frac{\log \eta_1 - \log \eta_3}{\log (a + t_3) - \log (a + t_1)}.$$

Writing the formula in the shape  $\eta = C / (1 + b t)^n$ , where  $C$  is the viscosity coefficient at  $0^\circ$ , the experimental results in the case of the whole series of liquids may be accurately represented by formulæ of the Slotte type by means of the following constants.

CONSTANTS IN SLOTTÉ'S FORMULA,  $\eta = C / (1 + b t)^n$ .

—	C.	b.	n.
Pentane .. .. .	·002827	·006039	1·7295
Hexane .. .. .	·003965	·005279	2·1264
Heptane .. .. .	·005180	·005551	2·1879
Octane .. .. .	·007025	·006873	2·0290
Isopentane .. .. .	·002724	·008435	1·2901
Isohexane .. .. .	·003713	·004777	2·3237
Isoheptane .. .. .	·004767	·005541	2·1633
Isoprene .. .. .	·002600	·006944	1·4433
Amylene .. .. .	·002534	·005341	1·7855
Diallyl .. .. .	·003388	·005780	1·9340
Methyl iodide .. .. .	·005940	·007444	1·4329
Ethyl iodide .. .. .	·007190	·006352	1·7520
Propyl iodide .. .. .	·009372	·007308	1·7483
Isopropyl iodide .. .. .	·008783	·006665	1·9161
Isobutyl iodide .. .. .	·011620	·009186	1·6577
Allyl iodide .. .. .	·009296	·007933	1·6592
Ethyl bromide .. .. .	·004776	·007212	1·4749
Propyl bromide .. .. .	·006448	·006421	1·8282
Isopropyl bromide .. .. .	·006044	·005916	2·0166
Isobutyl bromide .. .. .	·008234	·006187	2·1547
Allyl bromide .. .. .	·006190	·006895	1·7075

CONSTANTS IN SLOTTE'S FORMULA,  $\eta = C/(1 + bt)^n$ —continued.

—	C.	b.	n.
Ethylene bromide .. ..	•024579	•012375	1•6222
Propylene bromide .. ..	•023005	•011267	1•7075
Isobutylene bromide .. ..	•033209	•013227	1•7988
Acetylene bromide .. ..	•012307	•008905	1•5032
Bromine .. ..	•012535	•008935	1•4077
Propyl chloride .. ..	•004349	•004917	2•2453
Isopropyl chloride .. ..	•004012	•007485	1•5819
Isobutyl chloride .. ..	•005842	•007048	1•8706
Allyl chloride .. ..	•004059	•006366	1•7459
Ethylene chloride .. ..	•011269	•000933	1•6640
Ethylidene chloride .. ..	•006205	•007575	1•6761
Methylene chloride .. ..	•005357	•007759	1•4408
Chloroform .. ..	•007006	•006316	1•8196
Carbon tetrachloride .. ..	•013466	•010521	1•7121
Carbon dichloride .. ..	•01139	•007925	1•6325
Carbon bisulphide .. ..	•004294	•005021	1•6328
Methyl sulphide .. ..	•003538	•005871	1•6981
Ethyl sulphide .. ..	•005589	•006705	1•8175
Thiophen .. ..	•008708	•009445	1•6078
Dimethyl ketone .. ..	•003949	•004783	2•2244
Methyl ethyl ketone .. ..	•005383	•007177	1•7895
Methyl propyl ketone .. ..	•006464	•007259	1•8248
Diethyl ketone .. ..	•005949	•006818	1•8626
Acetaldehyde .. ..	•002671	•003495	2•7550
Formic acid .. ..	•029280	•016723	1•7161
Acetic acid .. ..	•016867	•008912	2•0491
Propionic acid .. ..	•015199	•009130	1•8840
Butyric acid .. ..	•022747	•010586	1•9920
Isobutyric acid .. ..	•018872	•009557	2•0059
Acetic anhydride .. ..	•012416	•010298	1•6831
Propionic anhydride .. ..	•016071	•011763	1•7049
Ethyl ether .. ..	•002864	•007332	1•4644

CONSTANTS IN SLOTTÉ'S FORMULA,  $\eta = C/(1 + bt)^n$ —continued.

—	C.	b.	n.
Benzene .. .. .	·009055	·011963	1·5554
Toluene .. .. .	·007684	·008850	1·6522
Ethyl benzene .. .. .	·008745	·008218	1·7616
Ortho-xylene .. .. .	·011029	·010379	1·6386
Meta-xylene .. .. .	·008019	·008646	1·6400
Para-xylene .. .. .	·008457	·008494	1·7326
Water—			
0° to 8° .. .. .	·017793	·017208	1·9944
0° to 100° .. .. .	·017944	·023121	1·5423
Methyl alcohol .. .. .	·008083	·006100	2·6793
Ethyl alcohol .. .. .	·017753	·004770	4·3731
Propyl alcohol .. .. .	·038610	·007366	3·2188
Butyl alcohol—			
0° to 52° .. .. .	·051986	·007194	4·2452
52° to 114° .. .. .	·056959	·010869	3·2150
Isopropyl alcohol—			
0° to 40° .. .. .	·045588	·007057	4·9635
40° to 78° .. .. .	·048651	·011593	3·4079
Isobutyl alcohol—			
0° to 38° .. .. .	·080547	·010840	3·6978
38° to 75° .. .. .	·085365	·011527	3·6708
75° to 105° .. .. .	·094725	·015838	3·0537
Inactive amyl alcohol—			
0° to 40° .. .. .	·085358	·008488	4·3249
40° to 80° .. .. .	·093782	·012520	3·3395
80° to 128° .. .. .	·152470	·026540	2·4618
Active amyl alcohol—			
0° to 35° .. .. .	·111716	·009851	4·3736
35° to 73° .. .. .	·124788	·015463	3·2542
73° to 124° .. .. .	·147676	·127583	2·0050
Trimethyl carbinol—			
20° to 50° .. .. .	·135060	·128156	1·8232
50° to 77° .. .. .	1·755458	·196967	2·0143
Dimethyl ethyl carbinol—			
0° to 27° .. .. .	·142538	·020868	3·2080
27° to 63° .. .. .	·154021	·027019	2·7578
63° to 95° .. .. .	·131901	·026082	2·6610
Allyl alcohol .. .. .	·021736	·009139	2·7925
Nitrogen peroxide .. .. .	·005267	·007098	1·7319
Methyl formate .. .. .	·004301	·014655	0·8325
Ethyl formate .. .. .	·005048	·007197	1·7006
Propyl formate .. .. .	·006679	·007179	1·9154

CONSTANTS IN SLOTTÉ'S FORMULA  $\eta = C/(1 + bt)^n$ —continued.

—	C.	b.	n.
Methyl acetate .. .. .	·004781	·006472	1·8636
Ethyl acetate .. .. .	·005783	·007384	1·8268
Propyl acetate .. .. .	·007706	·007983	1·8972
Methyl propionate .. .. .	·005816	·006820	1·8972
Ethyl propionate .. .. .	·006928	·007468	1·8914
Methyl butyrate .. .. .	·007587	·008081	1·8375
Methyl isobutyrate .. .. .	·006720	·007144	1·9405
Diethyl ether .. .. .	·002864	·007332	1·4614
Methyl propyl ether .. .. .	·003077	·006809	1·5863
Ethyl propyl ether .. .. .	·003969	·005454	2·1454
Dipropyl ether .. .. .	·005401	·006740	1·9734
Methyl isobutyl ether .. .. .	·003813	·005737	2·0109
Ethyl isobutyl ether .. .. .	·004826	·006549	1·9733

Slotte's formula gives the best results in the case of observed viscosity curves in which the slope varies but little with the temperature. As regards the relation between the chemical nature of the substances and the magnitude of their temperature coefficients, it is evident that—

(a) From the mode in which the constants  $n$  and  $b$  are derived, their individual values cannot be expected to be simply related to chemical nature.

(b) For the majority of the liquids the formula—

$$\eta = C/(1 + \beta t + \gamma t^2)$$

obtained from Slotte's formula by neglecting terms in the denominator involving higher powers of  $t$  than  $t^2$ , closely expresses the effect of temperature on viscosity, and in the formula the magnitudes of the coefficients  $\beta$  and  $\gamma$  are found to be definitely related to the molecular weight and constitution of the substances, except in the case of liquids which, like water and the alcohols, contain molecular aggregate.

In order to obtain quantitative relationships between viscosity and chemical nature, and to compare one group of substances with another, it is necessary to fix upon particular temperatures, and to obtain and compare the values corresponding with those temperatures. The first point to decide was at what temperatures viscosities should be compared. Inasmuch as the viscosity curves, even in the same family of substances, cross one another, it is obvious that quantitative relationships obtained at any single temperature of comparison, as has usually been done, can have no pretensions to generality. Following the method of Kopp, temperature of the boiling point may be considered as a comparable temperature, or we may adopt the

method indicated by Van der Waals; or, lastly, we may compare the viscosity values at the temperatures of equal slope, or at temperatures at which  $d\eta/dt$  is the same for the different liquids—that is, points at which temperature is exercising the same effect on viscosity.


Now, no matter which of these modes of comparison be instituted, definite general relations are apparent. Thus, if we compare the viscosity coefficients at the boiling points, it is found that as a homologous series is ascended the coefficients, as a rule, diminish. Of corresponding compounds, the one having the highest theoretical molecular has the highest coefficient. Normal propyl compounds have higher values than allyl compounds, and an iso-compound has a larger coefficient than a normal compound. In the case of other metameric substances, branching of the atomic chain and the symmetry of the molecule influence the magnitudes of the coefficients, the ortho-position in the case of aromatic compounds having a more marked effect than either the meta- or para-positions. There are, however, certain significant exceptions to the universality of these rules, but these are in all probability dependent upon differences in molecular complexity, as there is independent reason for believing that the anomalous liquids contain molecular aggregates. Very similar, although less definite, relationships are obtained at corresponding temperatures obtained by the method of Van der Waals, and these are still more obvious when the comparisons are made at temperatures of equal slope.

The attempt has been to ascertain if molecular viscosity can be expressed as the sum of partial effects which may be ascribed to the atoms and to the modes of atom linkage which occur in the molecule, and it has been found possible to obtain values for particular elements and groups, and to trace the special influence of the iso-grouping, of ring grouping, and of double linkage, upon the viscosity of a liquid in such manner as to obtain a very fair agreement between the observed and calculated value. Fundamental viscosity constants have thus been obtained for the various elements, and it is possible to assign a quantitative value to specific differences in molecular arrangement. Thus the fundamental viscosity constants at temperatures of equal slope may, for a particular slope, be expressed as follows:—

## FUNDAMENTAL VISCOSITY CONSTANTS.

Hydrogen.. .. .	H	44.5
Carbon .. .. .	C	31
Hydroxyl-oxygen .. .. C—O—H		166
Ether-oxygen .. .. C—O—C		58
Carbonyl-oxygen .. .. C=O		198

FUNDAMENTAL VISCOSITY CONSTANTS—*continued.*

Sulphur .. .. .	C—S—C		246
Chlorine (in monochlorides) .. .. .	Cl		256
Chlorine (in dichlorides) .. .. .	Cl'		244
Bromine (in monobromides) .. .. .	Br		372
Bromine (in dibromides) .. .. .	Br'		361
Iodine .. .. .	I		409
Iso grouping .. .. .	<		— 21
Double linkage .. .. .	(=)		48
Ring-grouping .. .. .	⊙		244

The following tables show the numbers calculated by means of these constants, together with those actually observed in a number of cases :—

—	Observed.	Calculated.	Difference per cent.
Pentane .. .. .	687	689	—0·3
Hexane .. .. .	818	809	1·1
Heptane .. .. .	931	929	—0·2
Octane .. .. .	1035	1049	—1·3
Isopentane .. .. .	663	668	—0·7
Isohexane .. .. .	799	788	1·4
Isoheptane .. .. .	908	908	0·0
Isoprene .. .. .	620	607	2·1
Diallyl .. .. .	728	729	—0·1
Methyl iodide .. .. .	638	664	—4·0
Ethyl iodide .. .. .	778	784	—0·8
Propyl iodide .. .. .	903	904	—0·1
Isopropyl iodide .. .. .	878	883	—0·6
Isobutyl iodide .. .. .	1010	1003	0·7
Allyl iodide .. .. .	864	866	—0·2
Ethyl bromide .. .. .	663	657	0·9
Propyl bromide .. .. .	774	777	—0·4
Isopropyl bromide .. .. .	750	756	—0·8
Isobutyl bromide .. .. .	877	876	0·1



—	Observed.	Calculated.	Difference per cent.
Allyl bromide .. .. .	734	739	-0.7
Ethylene bromide .. .. .	973	962	1.1
Propylene bromide .. .. .	1068	1082	-1.3
Isobutylene bromide .. .. .	1171	1181	-0.9
Acetylene bromide .. .. .	932	921	1.2
Propyl chloride .. .. .	658	661	-0.4
Isopropyl chloride .. .. .	644	640	0.6
Isobutyl chloride .. .. .	760	760	0.0
Allyl chloride .. .. .	617	623	-1.0
Ethylene chloride .. .. .	737	728	1.2
Methylene chloride .. .. .	600	600	0.0
Methyl sulphide .. .. .	578	575	0.5
Ethyl sulphide .. .. .	812	815	-0.3
Dimethyl ketone .. .. .	572	558	2.4
Methyl ethyl ketone .. .. .	671	678	-1.0
Methyl propyl ketone .. .. .	796	798	-0.2
Diethyl ketone .. .. .	785	798	-1.6
Acetaldehyde .. .. .	448	438	2.2
Formic acid .. .. .	456	484	-6.1
Acetic acid .. .. .	593	604	-1.8
Propionic acid .. .. .	712	724	2.4
Butyric acid .. .. .	842	844	-0.2
Isobutyric acid .. .. .	843	823	2.4
Acetic anhydride .. .. .	838	845	-0.8
Propionic anhydride .. .. .	1036	1085	-4.7
Ethyl ether .. .. .	635	627	1.3
Benzene .. .. .	688	697	-1.3
Toluene .. .. .	821	814	0.8
Ethyl benzene .. .. .	939	934	0.5
Ortho-xylene .. .. .	951	934	2.1
Meta-xylene .. .. .	939	934	0.5
Para-xylene .. .. .	923	934	-1.2

Those general results are, it should be stated, independent of the magnitude of the slope: no matter what particular value be selected, the relations are made obvious. Of course, in the actual comparison, such a value of the slope was selected as would comprehend the greatest number of observed cases.

In conclusion it may be pointed out that a comprehensive view of the physico-chemical relationships of a series of substances can only

be obtained by studying the variation of the physical property over as wide a range of temperature as possible; that the graphical or algebraical representation of the results so obtained will indicate whether particular members of a series are exceptional in behaviour as compared with their congeners; and if such exceptional behaviour occurs, it may be detected either in the viscosity-magnitude or the temperature, no matter whether we use the boiling point, a corresponding temperature, or a temperature of equal slope as the condition of comparison.

[T. E. T.]

Friday, April 1, 1898.

SIR EDWARD FRANKLAND, K.C.B. D.C.L. LL.D. F.R.S. Vice-President, in the Chair.

PROFESSOR DEWAR, M.A. LL.D. F.R.S. M.R.I.

*Liquid Air as an Analytic Agent.*

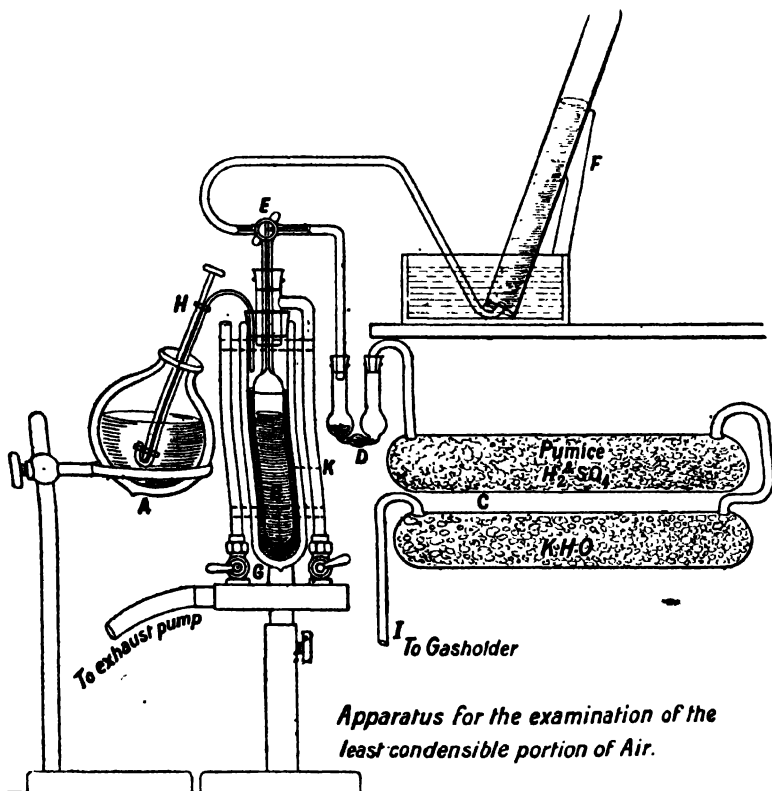
THE increasing importance of low-temperature research is shown by the gradual development of the applications of liquid air for scientific and other purposes. The much larger apparatus now used in the production of the liquid enables experiments to be made on a more imposing scale.

Liquid air poured from a tin can, filled by being dipped into a 5-gallon jar filled with the liquid, into a large silver basin heated to redness, remained apparently as quiescent at this high temperature as in cooler vessels, and maintained a spheroidal condition, just like other liquids. The temperature of the liquid air was about  $-190^{\circ}$  C., or  $83^{\circ}$  absolute, while the vessel in which it was placed had a temperature of  $800^{\circ}$  C., or  $1073^{\circ}$  Ab. In other words, between the wall of the silver vessel and the liquid air there was a difference of temperature of  $1000^{\circ}$  C., 12 times the absolute temperature of the liquid.

Liquid air can be of great service in the qualitative separation of mixtures of gases. With the object of ascertaining the proportion of any gas in air that is not condensable at about  $-210^{\circ}$  C. under atmospheric pressure, or is not soluble in liquid air under the same conditions, a series of experiments was made with the following apparatus.

A cylindrical bulb of a capacity of 101 c.c., marked B in figure, had a capillary tube sealed into it terminating in a three-way stop-cock, as shown at E. The parts marked C and D consist of soda-lime and sulphuric acid tubes for removing carbonic acid and water. The stand marked G holds the large vacuum test-tube into which B is inserted, and which contains liquid air maintained under continuous exhaustion. As this low temperature had to be kept steady from one to two hours, while at the same time the bulb B had to be completely covered with liquid air, it was necessary to arrange some means of keeping up the liquid air supply without disturbing the apparatus. The plan adopted is shown at H, which is a valve arrangement which can be so regulated as to suck liquid air from the large vacuum vessel A, and discharge it continuously along a pipe into the vacuum test-tube G, the latter being kept under good exhaustion. In working the apparatus, the tube I is connected to a gasometer containing 10 cubic feet of air, so that the volume of air condensed in each

experiment may be observed. This was generally from  $2\frac{1}{2}$  to 3 cubic feet. If there is a very small proportion of some substance not liquefiable or soluble in liquid air, then we should expect the vessel B would not fill up completely into the capillary tube. This is, however, exactly what does take place. After 40 minutes' cooling,



*Apparatus for the examination of the least condensable portion of Air.*

FIG. 1.

the vessel B and the cool part of the tube were filled with liquid. In this experiment some 80 litres of air were condensed, and any accumulated uncondensed matter must have been concentrated in the upper part of the capillary tube, which had a volume of 0.5 c.c. Under the conditions, therefore, the material looked for must be less than 1 part by volume in 180,000 of air.\*

\* These experiments, along with the succeeding ones on Bath Gas, were all described in a Paper entitled, 'Liquefaction of Air and the Detection of Impurities,' given at the Chemical Society on 4th November, 1897.

To test the working with an uncondensable gas added to air, a volume of 10 cubic feet was taken in the gasholder, and to that 500 c.c. of hydrogen were added. This is in the proportion of less than 1 in 500. Even after two hours' cooling, the tube B could only be filled four-fifths. In order to prove that the gas accumulated in the upper part of B was hydrogen, the three-way stopcock at E was turned, and the temperature allowed to rise, so that the gas was expelled from the evaporation of the liquid air and collected over mercury as shown at F. The gas thus collected was easily combustible and consisted chiefly of hydrogen. The amount of hydrogen was then reduced to 1 part in 1000 of air, and it was found that after one-and-a-quarter hours' cooling, the bulb B had filled to within a half c.c. of the capillary tube. A new sample of air containing 1 part of hydrogen in 10,000 of air, filled the bulb B completely as if it were ordinary air.

It appears from these experiments that 1 part of hydrogen in 1000 of air is just detectable in the form of an uncondensable residue. As the 80 litres of air condensed contained some 80 c.c. of hydrogen, it appears that 100 c.c. of liquid air at from  $-200^{\circ}$  to  $-210^{\circ}$  C. had dissolved nearly all this gas; in fact, that 20 c.c. of hydrogen at the low temperature is dissolved in 100 c.c. of liquid air, and can only be detected, by examining the first sample of gas boiled off or extracted by lowering the pressure on the liquid. In the paper on 'The Liquefaction of Air and Research at Low Temperatures,'\* it was shown that if hydrogen containing a small percentage of oxygen were employed for the purpose of getting a hydrogen jet, the liquid collected from it was oxygen, containing, however, so much hydrogen dissolved in it that the gas coming off for a time was explosive.

Coal gas, which is a mixture of hydrogen, marsh gas, carbonic oxide, and various illuminating gases and impurities, after passing through a coil of pipe surrounded with solid carbonic acid for the purpose of condensing the vapours of benzol, naphthalene, &c., when supplied to a tube similar to B, surrounded by boiling liquid air, gave a liquid and gaseous portion at the lowest temperature. It was possible to condense in this way all the constituents of coal gas, and to separate them after liquefaction by fractional distillation, except carbonic oxide and hydrogen.

Ultimately, however, the carbonic oxide would be condensed, and hydrogen be left alone in the gaseous state. Similarly, any gas less easily condensed than air could be separated from a mixture of the same with air. Hydrogen present in air to the extent of one in a thousand is just detectable, but smaller quantities escape direct observation owing to solution in the liquid. In order to press this inquiry a little further, some natural gas known to contain a different constituent, like helium, suggested itself as being worthy of trial. Lord Rayleigh's analysis of the gas from the King's Well, at Bath, gave

\* Proc., 1895, vol. xi. p. 221.

1·2 part of helium per 1000 volumes, so that it seemed admirably adapted for such experiments. By the kind permission of the Corporation of Bath, an abundant supply of this Gas was obtained for experimental purposes.

In a paper read before the Royal Society on December 19, 1833,\* by Dr. Daubeny, Professor of Chemistry at Oxford University, on the 'Quantity and Quality of the Thermal Springs of the King's Well in the City of Bath,' there are some interesting details. Dr. Daubeny's experiments extended over a month, and he estimated the volume of gas given off as from 80 to 530 cubic inches per minute (average 264). The temperature of the water of the King's Well was 115° Fahr., and the amount of water per minute was equal to 126 gallons. The average volume of gas was 240 cubic inches per minute. The gas was collected from an area of 20 feet in the centre of the bath; the maximum amount of gas obtained was 300 cubic inches, while the minimum quantity was 194 cubic inches per minute. Calculated at the rate of evolution of 250 cubic feet per day for 5000 years, then the whole gas given off amounts to 456 million cubic feet.

Thirty-two years after Daubeny's experiment Professor Williamson made a more elaborate examination of the Gases of the King's Well. In B.A. Reports, 1865, he gives the following as the volume composition of the gas:—

Carbonic Acid.	Oxygen.	Marsh Gas.	Nitrogen.
2·948	0·54	0·18	96·33
3·056	0·617	0·216	96·11

Williamson used a funnel 3 ft. 9 in. in diameter to collect the gas, and obtained a quantity equal to a rate of 112 cubic feet per day. This is only about half the amount Daubeny collected, and may be explained by the great alterations made in the bath itself between the dates of the observations.

In passing, it is interesting to note the general character of the saline constituents of the spring, as the most probable hypothesis is that the argon and helium come from the rocks traversed by the water. The following analysis was made by Dr. Attfield.

	Grs. per Gallon.				
Carbonate of calcium .. .. .	..	..	..	..	7·8402
Sulphate of calcium .. .. .	..	..	..	..	94·1080
Nitrate of calcium .. .. .	..	..	..	..	·5623
Carbonate of magnesium .. .. .	..	..	..	..	·5611
Chloride of magnesium .. .. .	..	..	..	..	15·2433
Chloride of sodium .. .. .	..	..	..	..	15·1555
Sulphate of sodium .. .. .	..	..	..	..	23·1400
Sulphate of potassium .. .. .	..	..	..	..	6·7020
Nitrate of potassium .. .. .	..	..	..	..	1·0540
Carbonate of iron .. .. .	..	..	..	..	1·2173
Silica .. .. .	..	..	..	..	2·7061

168·2898

Ramsay, the geologist, estimated the mineral ingredients obtained from this source in one year would equal a square column 9 feet in diameter and 140 feet high. Roscoe detected by spectroscopic examination the presence of lithium, strontium and copper. The sample of Bath gas examined by Rayleigh contained scarcely any oxygen and but little carbonic acid. The weight in a given globe of the N from the Bath gas (2.30522) is about half-way between that of chemical nitrogen (2.299) and "atmospheric" nitrogen (2.3101), suggesting that the proportion of argon is less than in air, instead of greater, as had been expected. Later experiments by Rayleigh proved that this nitrogen contained helium as well as argon.

The sample of gas from the Bath Spring was treated exactly in the same way as the hydrogen mixtures before referred to. During liquefaction there was a marked difference in the appearance of the liquefied gases, for while the hydrogen and air mixtures on condensation gave clear transparent liquids, the product from the Bath gas was turbid, and a precipitate gradually formed which by transmitted light looked yellowish-brown. The yellowish-brown precipitate is a hydro-carbon, probably of the petroleum series, having a marked aromatic smell, and is liquid at the ordinary temperatures. It was probably this gas which Professor Williamson gave as marsh gas in his analysis. Further research will be made on this substance. Another peculiarity of the liquid nitrogen obtained from Bath gas is that, on examining it with a spectroscope, even through a thickness of two inches of liquid, no trace of the characteristic oxygen absorption spectrum could be obtained. In all other attempts to make nitrogen for liquefaction on the large scale, oxygen could always be detected in the liquid by means of its absorption spectrum. Another phenomenon was that the gas from the King's Well could not be entirely condensed by refrigeration with liquid air boiling *in vacuo*. After the cooling had continued for some time, the gas ceased to flow into the condensing vessel, and the upper part of the vessel was occupied by a gas that would not undergo liquefaction at the temperature together with substantially liquid nitrogen saturated with the said gas.

About 70 litres of the Bath gas were condensed, certainly the largest quantity of this gas ever subjected to chemical examination. This was boiled off, and as by accident too much nitrogen had volatilised along with the gas, oxygen was added, and the mixture sparked over alkali, to get rid of the excess of nitrogen. The sample of gas directly collected from the liquid nitrogen contained about 50 per cent. of helium. During the sparking the helium lines were well marked (along with others, the origin of which must be settled later), and a vacuum tube filled with the product of the sparking gave a splendid spectrum of the gas. The recorded unknown lines in the Bath helium were subsequently detected along with helium in the more volatile portion of liquid air.\* Eight months after my paper to the Chemical Society, and some two months after this address was

\* See 'Nature,' vol. lviii. p. 570, Letter of Sir William Crookes, Oct. 11, 1898.

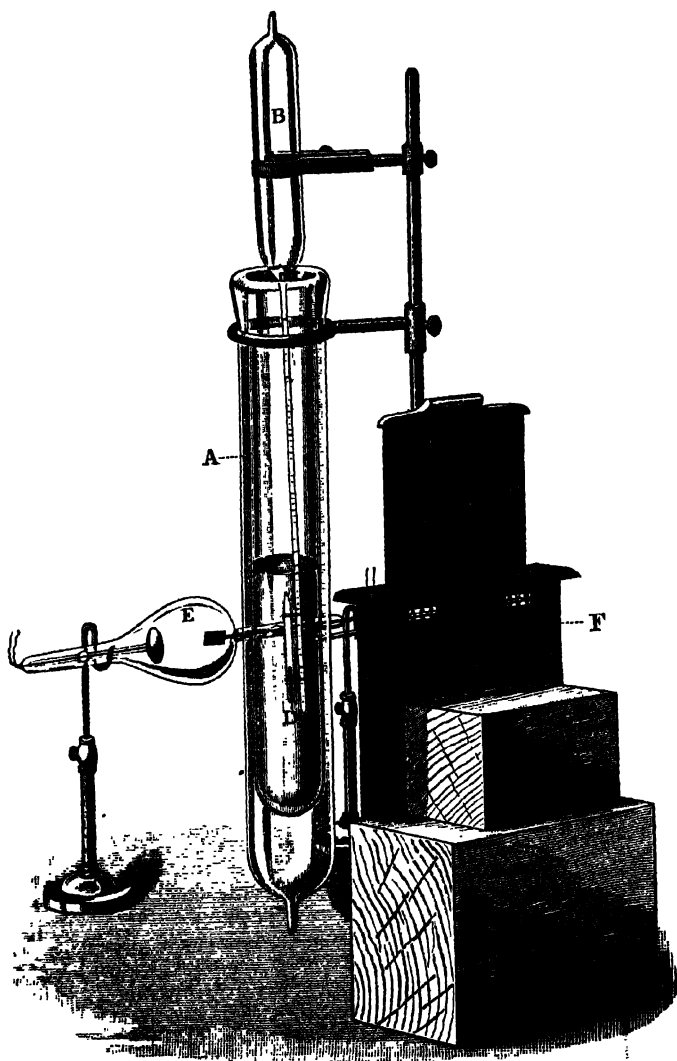


FIG. 2.

A, glass vacuum vessel, containing liquid air. B, tube of argon. C, tube of liquid chlorine. D, tube of metallic sodium. E, Röntgen X-ray bulb. F, photographic plate behind sheet aluminium.



delivered, the same material was found by Professors Ramsay and Travers to exist in argon, and has been recognised and named by them Neon, a new element.

It is, therefore, possible to separate helium from other gases by liquefaction when it is only present to the extent of one part in one thousand. From this it would appear that helium is less soluble in liquid nitrogen than hydrogen in liquid air, and is of greater volatility than the constituents of the other gases which were condensed. If the sample of the uncondensed gas from the first liquefaction of the Bath gas were again treated in the same way, a much more concentrated specimen of helium could be obtained. Provided helium were wanted on a large scale, then a liquid air apparatus, similar to that in use at the Royal Institution, transported to Bath, and worked with the gas from the King's Well, could be made to yield a good supply, as the gas contains 1.2 parts in 1000.

Argon, which is present in the proportion of 1.4 per cent., condenses with the nitrogen; but if the liquid be allowed to slowly boil away, a residuum may be obtained containing about 7 per cent. of argon. Argon, when frozen, solidifies to a perfectly clear glass.

#### ABSORPTION OF RÖNTGEN RADIATION AT LOW TEMPERATURE BY DIFFERENT BODIES.

The transparency of bodies to the Röntgen radiation is an interesting study, although we are not in a position to draw definite conclusions from the results. As a general fact we know the opacity of elements in the solid state increases with the atomic weight.

In the experiments small tubes of the same bore were filled respectively with liquid argon and chlorine, potassium, phosphorus, aluminium, silicon and sulphur, and exposed at the temperature of liquid air (in order to keep the argon and chlorine solid) in front of a photographic plate shielded with a sheet of aluminium to an X-ray bulb (see Fig. 2). The order of increasing opacity of the shadow of each substance was observed, and the sequence in the list given above represents the results. A tube containing silicon was a little more transparent than the potassium or chlorine. Sodium and liquid oxygen and air, nitrous and nitric oxides proved much more transparent than chlorine. Tubes of potassium, argon and liquid chlorine presented no very marked difference of density on the photographic plates.

From these experiments it would appear that argon is relatively more opaque to the X-rays than either oxygen, nitrogen, or sodium, and that it is on a level with potassium, chlorine, phosphorus, aluminium and sulphur. This may be regarded as supporting the view that the atomic weight of argon is twice its density relative to hydrogen.

#### THERMAL TRANSPARENCY AT LOW TEMPERATURES.

Pictet, after an elaborate investigation, concluded that below a certain temperature all substances had practically the same thermal

transparency, and that a non-conducting body became ineffective at low temperatures in shielding a vessel from the influx of heat. Experiments, about to be detailed, however, prove that such is not the case, the transference of heat observed by Pictet appearing to be due not so much to the materials themselves as to the air contained in their interstices. Good exhaustion in the ordinary vacuum vessels used in low temperature work reduces the influx of heat to one-fifth of what is conveyed when the annular space of such double-walled vessels is filled with air. If the interior walls are silvered, or excess of mercury is allowed to remain, the influx of heat is diminished to one-sixth of the amount entering without the metallic coating. The total effect due to the high vacuum and silvering is to reduce the ingoing heat to one-thirtieth of the original amount, i.e. roughly, to  $3\frac{1}{2}$  per cent.

By filling the annular space between the walls of several similar vacuum vessels with various substances, and exhausting them all to the same low pressure, large differences in the thermal isolation were observed. The rate of evaporation of equal volumes of liquid air contained in the respective vessels measures the rate of influx of heat. Moreover, it appears that what might be called under the circumstances the thermal transparency of some materials diminished at very low temperatures instead of increasing, as had been asserted. Thus, of two vacuum tubes (one simply exhausted, and the other having powdered carbon in the vacuum space), the latter, at low temperature, was the most efficient preserver of liquid air, showing that the carbon diminished the radiation and gas convection. But when the vacuum was destroyed and air admitted into the space, the liquid air in the carbon tube boiled off much more vigorously than that in the simple tube, indicating that at ordinary temperatures carbon allowed more heat to pass than did air.

In conducting these experiments, generally sets of three double-walled glass tubes, as nearly identical in size and shape as possible, were mounted on a common stem, and two out of the three filled with different kinds of powders, while the third is left empty as a standard for comparison (Fig. 3). In this way each set had the same vacuum, and as intercommunication between the tubes after sealing off from the pump was left free, any deterioration in the vacuum on keeping affected all three vacuum tubes to the same extent.

The preparation of such tubes entails enormous labour, because it takes days of exhaustion with a mercurial pump to extract the occluded gases, even at as high a temperature as the glass would stand. Before beginning the experiment, the vacuum tubes of each triple set were filled with liquid air, and allowed to stand half an hour in order to get the heat conduction in the porous mass into a steady state. The tubes after this treatment were filled to the same height, and the relative times required to distil off the same volume of liquid air from each observed—the outer surface of the vacuum tubes being maintained at a steady temperature by immersion in a large vessel of water. Neither the tubes nor the shape of the vacuum space

in each were absolutely identical, so that the results are simply comparative. The general ratio of heat propagation found for two substances when different sets of double-walled tubes of about the same form and proportion were compared, remained substantially

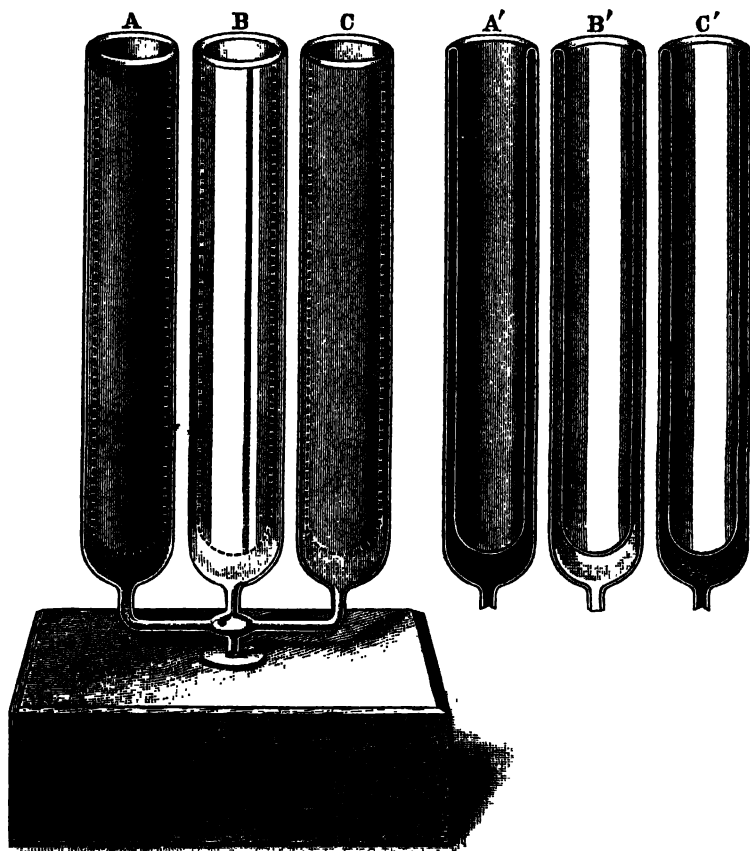


FIG. 3.—Three tubes blown on to one stem, so that the exhaustion in each would be identical.

A, filled with lamplblack between the inner and outer tubes. B, annular space left empty. C, filled with silica between the tubes. A', B', C', the same tubes in section.

constant when a high vacuum was reached. A confirmation of the results was generally made by noting the time required to evaporate the whole of the air from each tube. The annular vacuum space had generally a thickness of 4 to 5 mm., and was in each case completely filled up with the solid. In reality, however, the absolute



glass surface maintained at a higher temperature. To separate the true conduction from the radiation and the gas motion would require far more elaborate experiments, but these are sufficient to prove that the presence of certain finely divided solids in the high vacuum space

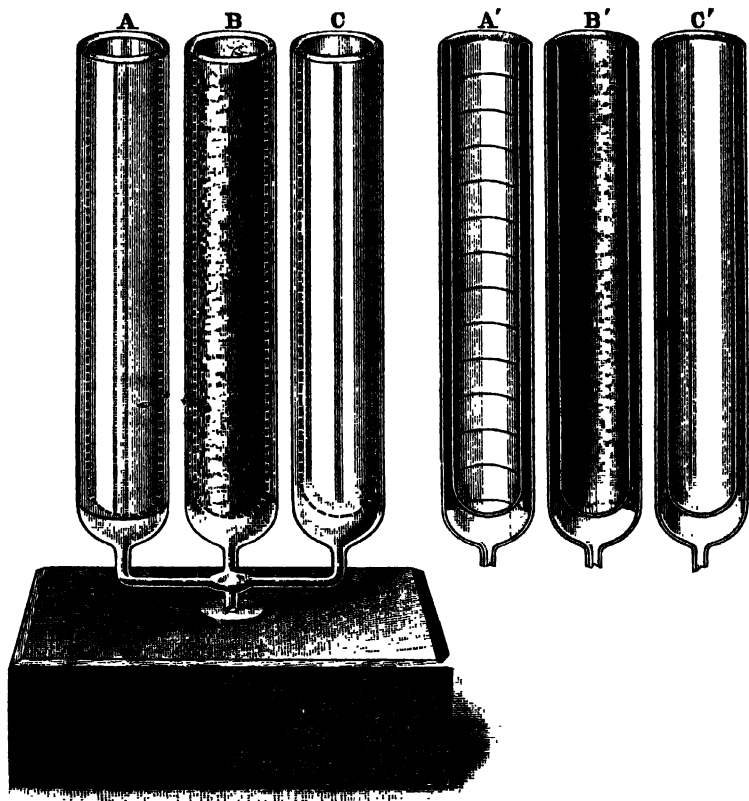


FIG. 4.—Three tubes blown on to one stem, similar to Fig. 3.

A, vacuum space having three turns of gold paper, gold outside. B, vacuum space having some pieces of gold leaf put in so as to make contact between walls of vacuum tube. C, vacuum space empty. A', B', C', the same tubes in section.

of the vessels used in low temperature research improves the heat insulation, while in the presence of air the same bodies facilitate the transference of heat. This is the explanation of Pictet's apparently extraordinary results.

In no case was the diminution of the influx of heat, in the case of



### PHOTOGRAPHIC ACTION AT THE TEMPERATURE OF LIQUID AIR.

In a former lecture on Phosphorescence and Photographic Action, it was shown that photographic action was reduced by 80 per cent. at the temperature of  $-182^{\circ}\text{C}$ . It was further proved that a sensitive film was still comparatively active at the temperature of  $-210^{\circ}\text{C}$ . Experiments in this direction have been continued at different times.

In these new experiments the source of light was respectively a 16 candle-power lamp, a magnesium and cadmium spark discharge, and a Röntgen bulb. Small dark slides were prepared having a circular hole. One was placed in liquid air, and another simultaneously exposed for the same time at the ordinary temperature (Fig. 7). They were developed together, and the density of the image observed (Fig. 5).

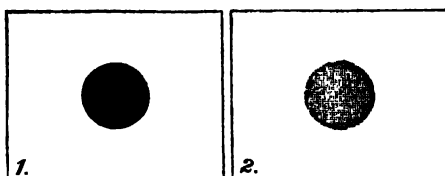


FIG. 5.

1, photographic film exposed at ordinary temperature. 2, photographic film cooled in liquid air during exposure.

Both were exposed for the same length of time, and both were developed together.

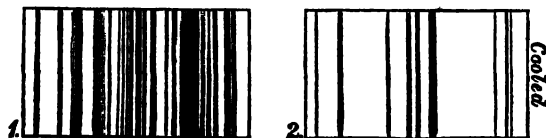


FIG. 6.—Ultra-violet spectrum of spark discharge.

1, on film at ordinary temperature. 2, on film cooled in liquid air.

Both exposed for the same length of time and then developed together.

### DISTANCE OF PLATES FROM SOURCE OF LIGHT GIVING THE SAME PHOTOGRAPHIC INTENSITY.

Source of Light.	Cooled Plate.	Uncooled Plate.	Ratio of Intensities at Balance.
16 candle-power lamp .. .. .	in. 20	in. 50	1 to 6
Ultra-violet spark magnesium and cadmium .. .. .	22½	90	1 to 16
Röntgen bulb .. .. .	10	24½	1 to 6

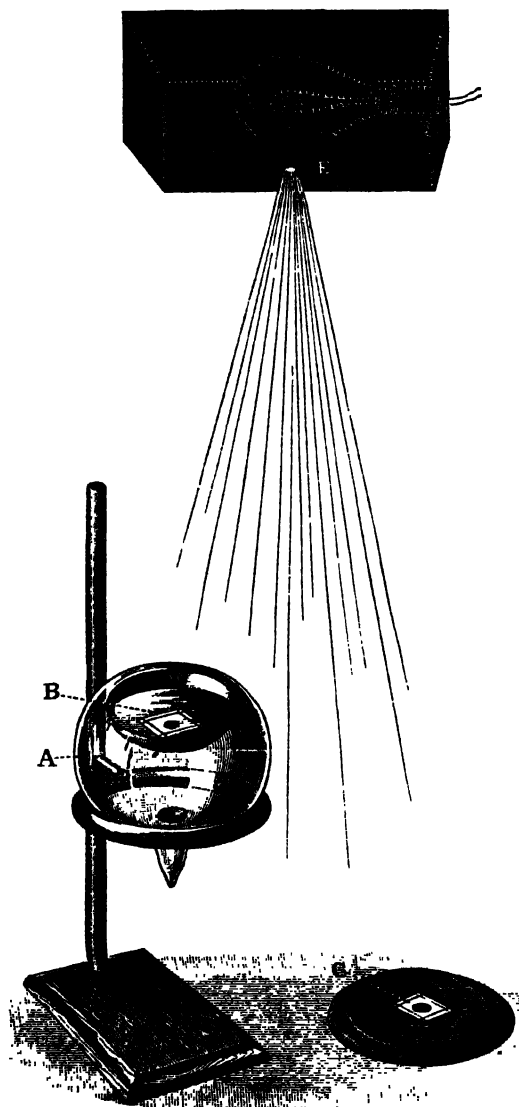


FIG. 7.

A, vacuum cup with liquid air, into which is placed a photographic film in a small metallic slide having a hole in the centre. C, a metallic slide, holding a photographic film, which is exposed at ordinary temperature.

Both of these are exposed to the light from a 16 candle-power lamp D, contained in a box. The light is diminished or increased by the diaphragm at E.



Further trials were made by bringing the cooled plate nearer to the source of light until finally a position was found where the very feeble photographic impression that appeared on both plates had the same density. In this position the relative distances of the plates from the source of light were measured. This mode of conducting the photographic comparison of the hot and cold plates gets over the difficulty of variation in the intensity of the source of light. From these experiments it would appear that when cooled to the temperature of liquid air both the incandescent lamp and the Röntgen radiation were reduced to 17 per cent. of their photographic action at the ordinary temperature; whereas the ultra-violet radiation was reduced to about 6 per cent. This marked increase in the inertia of the photographic plate at low temperatures for the short wave-lengths cannot be explained by the absorption of liquid air, for such radiation as this is small for a thickness of 10 to 20 mm. of the liquid. It is possible that the ultra-violet radiation is dissipated by the photographic film at low temperatures to a greater extent than with ordinary light, through absorption and subsequent emission as a phosphorescent glow. It would seem probable that if the plate could be developed at these low temperatures no action would be apparent, and that it is during the heating up after the low temperature exposure that the photographic action on the film takes place through an internal phosphorescence. This possibility must make us cautious in drawing inferences as to possible chemical action at low temperatures.

A more elaborate study of photographic and phosphorescent effects at low temperatures would add much to our knowledge of the chemical and physical actions of light.

Friday, April 29, 1898.

BASIL WOODD SMITH, Esq. F.R.A.S. F.S.A. Vice-President,  
in the Chair.

PROFESSOR ANDREW GRAY, M.A. LL.D. F.R.S.

*Magneto-Optic Rotation and its Explanation by a Gyrostatic Medium.*

THE action of magnetism on the propagation of light in a transparent medium has been rightly regarded as one of the most beautiful of Faraday's great scientific discoveries. Like most important discoveries it was no result of accidental observation, but was the outcome of long and patient inquiry. Guided by a conviction that (to quote his own words) "the various forms under which the forces of matter are made manifest have one common origin," he made many attempts to discover a relation between light and electricity, but for very long with negative results. Still, however, retaining a strong persuasion that his view was correct, and that some such relation must exist, he was undiscouraged, and only proceeded to search for it more strictly and carefully than ever. At last, as he himself says, he "succeeded in magnetising and electrifying a ray of light, and in illuminating a magnetic line of force."

Faraday pictured the space round a magnet as permeated by what he called lines of force; these he regarded as no mere mathematical abstractions, but as having a real physical existence represented by a change of state of the medium brought about by the introduction of the magnet. That there is such a medium surrounding a magnet we take for granted. The lines of force are shown by the directions which the small elongated pieces of iron we have in iron filings take when sprinkled on a smooth horizontal surface surrounding a horizontal bar magnet, as in the experiment I here make. [*Experiment to show field of bar magnet by iron filings.*]

The arrangement of these lines of force depends upon the nature of the magnet producing them. If the magnet be of horse-shoe shape the lines are crowded into the space between the poles; and if the pole faces be close together and have their opposed surfaces flat and parallel, the lines of force pass straight across from one surface to the other in the manner shown in the diagram before you. [*Diagram of field between flat pole faces.*]

The physical existence of these lines of force was demonstrated for a number of different media by the discovery of Faraday to which

I have already referred, and on which almost all the later work on the relation of magnetism to light has been founded. I am permitted by the kindness of the authorities of this Institution to exhibit here the very apparatus which Faraday himself employed, though for the various experiments I have to make it is necessary to actually use another set of instruments. [*Apparatus shown.*] Before repeating Faraday's experiment, let me describe shortly what I propose to do, and the effect to be observed.

A beam of plane polarised light is produced by passing white light from this electric lamp through a Nicol's prism. To understand the nature of plane polarised light, look for a moment at this other dia-

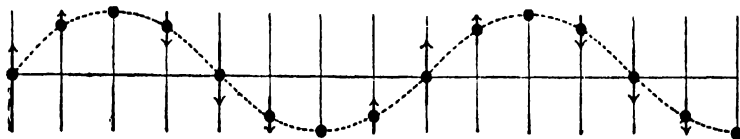


FIG. 1.

gram (Fig. 1). It represents a series of particles displaced in a certain regular manner to different distances from the mean or equilibrium positions they originally had along a straight line. They are moving in the directions shown by the arrows and with velocities depending on their positions, as indicated by the lengths of the arrows. Suppose a certain interval of time to elapse. The particles will have moved in that time to the positions shown in this other diagram (Fig. 2), on

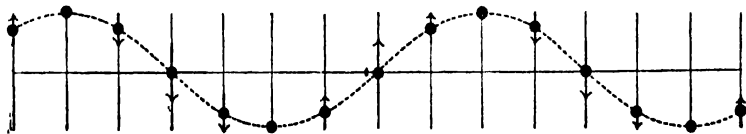


FIG. 2.

the same sheet. It will be seen that the velocities as well as the positions of the particles have altered, but that the configuration is the same as would be given by the former diagram moved through a certain distance to the left.

Thus an observer looking at the particles and regarding their configuration would see that configuration apparently move to the left, and this, it is very carefully to be noted, is a result of the transverse motions of the individual particles. In another interval of time equal to the former, the arrangement of particles will appear to have moved a further distance of the same amount towards the left.

This transverse motion of the particles, thus shown displaced from

their equilibrium positions, represents the vibration of the medium which is the vehicle of light, and the right to left motion of the configuration of particles is the wave motion resulting from that vibration. I do not say that the medium is thus made up of discrete particles, or that the different portions of it vibrate in this manner, but there is undoubtedly a directed quantity transverse to the direction in which the wave is travelling, the value of which at different points may be represented by the displacements of the particles, and which varies in the same manner, and results, as here shown, in the propagation of a wave of the quantity concerned.

In fact we have here a representation of a wave of plane polarised light. The directions of vibration are right lines parallel at all points along the wave. Ordinary light consists of vibrations the directions of which are not parallel if rectilinear, and each vibration is therefore capable of being resolved into two in directions at right angles to one another. The Nicol's prism in fact splits a wave of ordinary unpolarised light into two waves, one in which the vibrations are in one plane containing the direction in which the light is travelling, the other in a plane containing the same direction, but at right angles to the former. One of these waves is stopped by the film of Canada balsam in the prism and thrown out of its course, while the other wave is allowed to pass on undisturbed.

If the wave thus allowed to pass by one Nicol's prism be received by another, it is found that there are two positions of the latter in which the wave passes freely through the second prism, and two others in which the wave is stopped. The prism can be turned from one position to another by properly placing it and then turning it round the direction of the ray. It is found that if the prism be thus turned

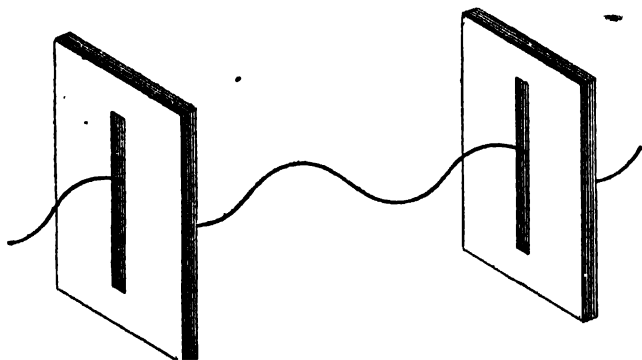


FIG. 3.

from a position in which the light is freely transmitted, we come after turning it through  $90^\circ$  to a position in which the light is stopped, and that if we go on turning through another angle of  $90^\circ$  a position

is reached in which the light is again freely transmitted, and so on, the light being alternately stopped and transmitted by the second prisms in successive positions  $90^\circ$  apart.

The mode of passage of the wave by the Nicols when their planes are parallel, and its stoppage when the planes are crossed, are illustrated by this diagram (Fig. 3) of a vibrating cord and two slits. When the slits are parallel, the vibration which is passed by one is passed by the other; when they are crossed, a vibration passed by one is stopped by the other.

Two planes of symmetry of the prisms parallel to the ray, and called their principal planes, are parallel to one another when the light passes through both, and are perpendicular to one another when the light passed by the first is stopped by the second. We shall call the first prism the polarising prism, or the *polariser*, from its effect in producing plane polarised light; the other, the *analyser*. The stoppage of the light in the two positions  $180^\circ$  apart of the second prism, and its passage in the two intermediate positions, show that the light passed by the first prism is plane polarised.

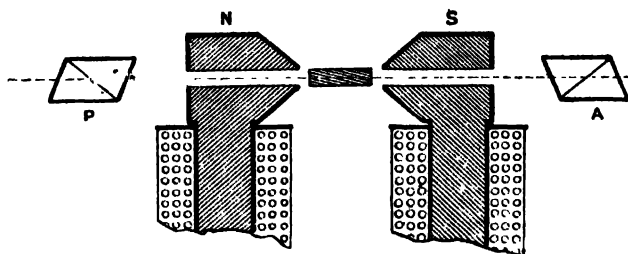


FIG. 4.

Now a beam of plane polarised light is passed through the perforated pole-pieces of this large electro-magnet (Fig. 4), so that the beam travels between the pole-faces along the direction which the lines of force there would have if the magnet were excited by a current. The arrangement of the apparatus is as shown in the diagram. The light is polarised by the prism P, passes through the magnetic field, and then through the analysing prism A, to the screen. As you see, when the second prism is turned round the ray the light on the screen alternately shines out and is extinguished, and you can see also that the angle between the positions of free passage and extinction is  $90^\circ$ .

I now place in the path of the beam this bar of a very remarkable kind of glass, some of the properties of which were investigated by Faraday. It is a very dense kind of lead glass, which may be described as a silicated borate of lead; that is, it contains silica, boric acid and lead oxide. The beam is not disturbed although the light passes through the glass from end to end. I now adjust the analysing prism to very nearly complete extinction, and then excite the magnet.

If the room is sufficiently darkened, I think all will see that when the magnet is excited there is a very perceptible brightening of the dim patch of light on the screen, and that this brightening disappears when the current is removed from the magnet. This is Faraday's discovery.

How are we to describe this result? What effect has been produced by the magnetic field? It is clear that the direction of vibration of the light emerging from the specimen of heavy glass has been changed relatively to the prism so that the light now readily passes. It is found, moreover, that the amount of turning of the direction of vibration round the ray is proportional to the length of the specimen, so that the directions of vibration at different points along the wave within the specimen lie on a helically twisted surface, and may be regarded as represented by the straight rods in the model before you on the table (Fig. 5).

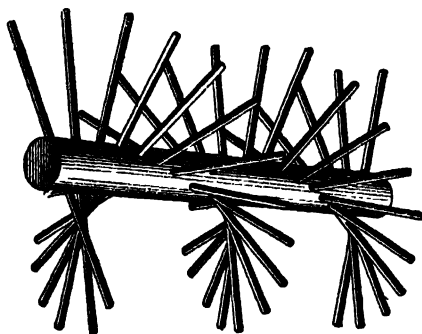


FIG. 5.

It is also found that the amount of the turning depends on the intensity of the magnetic field—is, in fact, simply proportional to that intensity. Hence the turning is proportional to the mean intensity of the field, and to the length of the path in the medium, that is, to the product of these two quantities. It also depends on the nature of the medium. The angle of turning produced by a field of known intensity when the ray passes through bisulphide of carbon has been very carefully measured by Lord Rayleigh, whose results are of great value for other magnetic work.

The law of proportionality of the amount of turning of the plane of polarisation to the intensity of the magnetic field in the space in which the substance is placed, is not, however, to be regarded as established for strongly magnetic substances, such as iron, nickel or cobalt. The matter has not yet been completely worked out, but the turning in such cases seems to be more nearly proportional to the intensity of magnetisation, a different quantity from the intensity of the magnetic field producing the magnetisation. If this law be

found correct, the angle of turning will be proportional to the product of the intensity of magnetisation and to the length of the path; and the angle observed divided by this product will give another constant, which has been called Kundt's constant.

The rotation of the plane of polarisation in strongly magnetised substances was investigated by Kundt, the very eminent head of the Physical Laboratory of the University of Berlin, who died only a year or two ago. Kundt is remembered for many beautiful methods which he introduced into quantitative physical work; but no work he did was more remarkable than that which he performed in magneto-optic rotation when he succeeded in passing a beam of plane polarised light through plates of iron, nickel and cobalt. Such substances, though apparently opaque to light, are not really so when obtained in plates of sufficient thinness. In sufficiently thin films all metals, so far as I know, are transparent, not merely to Röntgen rays, but to ordinary light. Kundt conceived the idea of forming such films of the strongly magnetic metals, so as to investigate their properties as regards magneto-optic rotation. He succeeded in obtaining them by electroplating platinised glass with such thin strata of these metals that light passed through them in sufficient quantity for observation. The rotation produced by the glass and the exceedingly thin film of platinum was determined once for all and allowed for. Kundt obtained the remarkable result that the magnetic rotatory power in iron is so great, that light transmitted through a thickness of one centimetre of iron magnetised to saturation is turned through an angle of over  $200,000^\circ$ , that is, that light passing through a thickness of an inch of iron magnetised to saturation would have its plane of polarisation turned completely round more than a thousand times; in other words, one complete turn would be given by a film less than  $\frac{1}{1000}$  of an inch in thickness. A scarcely smaller result has been found by Du Bois for cobalt, and a maximum rotation of rather less than half as much by the same experimenter for nickel.

The direction of turning in all the cases which have so far been specified—that is, Faraday's glass, bisulphide of carbon, iron, nickel and cobalt—is the same as that in which a current of electricity would have to flow round the spires of a coil of wire surrounding the specimen so as to produce the magnetic field. This we call the *positive* direction. There are, however, many substances in which the turning produced by the magnetic field is in the contrary or negative direction; for example, ferrous and ferric salts of iron, chromate and bichromate of potassium, and in fact most compound substances which are feebly magnetic.

Faraday established by his experiments the fact that substances fall into two distinct classes as tested by their behaviour under the influence of magnetic force. For example, an elongated specimen of iron, nickel or cobalt, if freely suspended horizontally between the poles of our electro-magnet, would set itself with its length along the lines of force. On the other hand, a similar specimen of heavy glass, or a

tube filled with bisulphide of carbon, would, if similarly suspended, set itself across the lines of force. The former substances were therefore called by Faraday paramagnetic, the latter diamagnetic.

It might be supposed that diamagnetics would show a turning effect opposed to that found in paramagnetics, but this is not the case. As we have seen, bisulphide of carbon and heavy glass, which are diamagnetics, show a turning in the same direction as that produced in iron—as indeed do most solid, fluid and gaseous diamagnetics. Feebly paramagnetic compound substances, on the other hand, produce negative rotation.

A theory of diamagnetism has been put forward in which the phenomena are explained by supposing that all substances are paramagnetic in reality, but that so-called diamagnetic bodies are less so than the air in which they are immersed when experimented on. Thus the diamagnetic quality is one of the substances relatively to air, in the same kind of way as the apparent levity of a balloon is due to the fact that its total weight has a positive value, but is less than that of the air displaced by the balloon and appendages. Lord Kelvin's dynamical explanation of magneto-optic rotation does not bear out this view of the matter.

Before passing to the dynamical explanation, however, I must very shortly call attention to some remarkable discoveries in this subject made by Dr. John Kerr, of Glasgow. I have here an electro-magnet arranged as in the diagram before you (Fig. 6). The light from the lamp is first plane polarised by the Nicol P, then it is thrown on the piece of silvered glass G, and part of it is thereby reflected through this perforated pole-piece so as to fall normally on the polished point of the other pole-piece. Reflection thus takes place at perpendicular incidence, and the reflected light is received by this second Nicol. When the magnet is unexcited the second Nicol is arranged so as to quench the reflected light. The magnet is then excited, and it is found that the light is faintly restored, showing that an effect on the polarisation of the

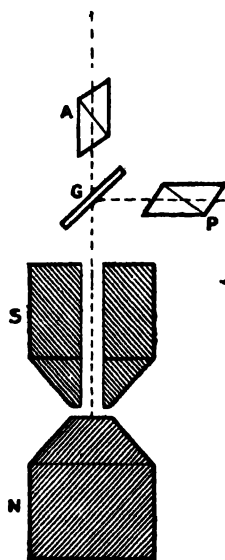


FIG. 6.

light has been produced by the magnetisation. It is to be noticed here that the incident and reflected light is in the direction of magnetisation. We shall not pause to make this experiment. It was arranged this morning and successfully carried out; but the effect is slight, and might not be noticeable without precautions,



which we have hardly time to make, to exclude all extraneous light from the screen.

It would perhaps be incorrect to say that the plane of polarisation has been rotated in this case, as it has been asserted by Righi that the light after reflection is no longer plane polarised, but that there are two components of vibration at right angles to one another, so related that the resultant vibration is not rectilinear but elliptical. There is therefore no position in which the analysing prism can be placed so as to extinguish the reflected light. The transverse component necessary to give the elliptic vibration is, however, in this case, if it exists, very small, and very nearly complete extinction of the beam can be obtained by turning the analysing prism round so as to stop the other component vibration. The angle through which the prism must be turned to effect this is the amount of the apparent rotation. The direction of rotation is reversed by reversing the magnetism of the reflecting pole. Dr. Kerr found that the direction is always that in which the current flows in the coils producing the magnetisation of the pole.

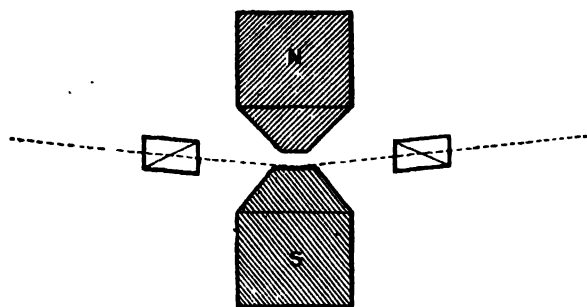


FIG. 7.

Dr Kerr also made experiments with light obliquely incident on a pole-face, with the arrangement of apparatus shown in this other diagram (Fig. 7). He found that the previously plane polarised light was by the reflection rendered slightly elliptically polarised. A slight turning of the analysing Nicol was necessary to place it so as to stop the vibration corresponding to the long axis of the ellipse and so secure imperfect extinction.

These effects are, like those of normal incidence, very small, and they can hardly be shown to an audience.

I must now endeavour to give some slight account of the theories that have been put forward in explanation of magneto-optic rotation. There is an essential distinction between it and what is sometimes called the natural rotation, the plane of polarised light produced by substances, such as solutions of sugar, tartaric acid, quartz, &c., some of which rotate the plane to the right, some to the left. When

light is sent once along a column of any of those substances without any magnetic field, its plane of rotation is rotated just as it is in heavy glass or bisulphide of carbon in a magnetic field. But if the ray, after passing through the column of sugar or quartz, is received on a silvered reflector and sent back again through the column to the starting point, its plane of polarisation is found to be in the same direction as at first. Quite the contrary happens when the rotation is due to the action of a magnetic field. Then the rotation is found to be doubled by the forward and backward passage, and it can be increased to any required degree by sending the ray backward and forward through the substance, as shown in this other diagram (Fig. 8).

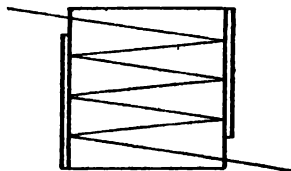


FIG. 8.

Thus the rotations in the two cases are essentially different, and must be brought about by different causes. In fact, as was first, I believe, shown by Lord Kelvin, the annulment of the turning in quartz, and the reinforcement of the turning in a magnetic field, produced by sending the ray back again after reflection at the surface of an optically denser medium, points to a peculiarity of structure of the medium as the cause of the turning of the plane of polarisation in sugar solutions and quartz, and to the existence of rotation in the medium as the cause of the turning in a magnetic field. Think of an elastic solid, highly incompressible and endowed with great elasticity of shape and of the same quality in different directions—a stiff jelly may be taken as an example to fix the ideas. Now let one portion of the jelly have bored into it a very large number of extremely small corkscrew-shaped cavities, having their axes all turned in the same direction. Let another portion have imbedded in it a very large number of extremely small rotating bodies, spinning-tops or gyrostats in fact, and let these be uniformly distributed through the substance, and have their axes all turned in the same direction.

Both portions would transmit a plane polarised wave of transverse vibration travelling in the direction of the axes of the cavities or of the tops with rotation of the plane of polarisation; but in the former case the wave, if reflected and made to travel back, would have the original plane of polarisation restored; in the latter the turning would be doubled by the backward passage.

To understand this it is necessary to enter a little in detail into the analysis of the nature of plane polarised light. As I have already said, the elastic solid theory may not express the facts of light propagation, but only a certain correspondence with the facts. But its use puts this matter in a very clear way. In a ray of plane polarised light each portion of the ether has a motion of vibration in a line at right angles to the ray, and the direction of this line is the

same for each moving particle. The lines of motion and the relative positions of the particles in a wave are shown in the first diagram above (Fig. 1). As the motion is kept up at the place of excitation it is propagated out by the elastic resistance of the medium to displacement, and the configuration of particles travels outwards with the speed of light, traversing a wave-length (represented in the diagram by the distance between two particles of the row in the same phase of motion) in the period of complete to-and-fro motion of a particle in its rectilinear path.

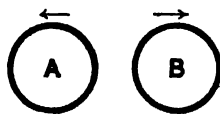


FIG. 9.

Now, a to-and-fro motion such as this can be conceived as made up of two opposite uniform and equal circular motions. Think of two distinct particles moving in the two equal circles A B in this diagram (Fig. 9), with equal uniform speeds in opposite directions. Let each particle be at the top of its

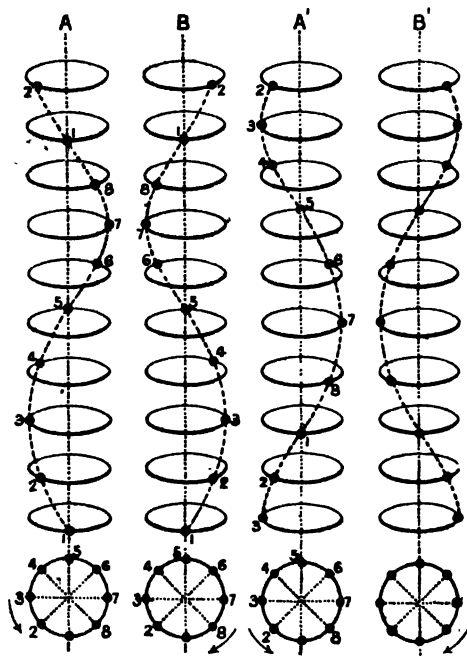


FIG. 10.

circle at the same instant; then at any other instant they will be in similar positions, but one on the right, the other on the left of the vertical diameter of the circle. Thus at that instant each particle is moving downward or upward at the same speed, while with whatever speed one is moving to the left, the other is moving with precisely

that speed towards the right. Imagine, now, these two motions to be united in a single particle. The vertical motions will be added together, the right and left motions will cancel one another, and the particle will have a motion of vibration in the vertical direction of range equal to twice the diameter of the circles, and in the period of the circular motions.

The rate of increase of velocity of the particle at each instant is the resultant obtained by properly adding together the accelerations of the particles in the circular motions, and therefore the force which must act on the particle to cause it to describe the vibratory motion just described, is the resultant of the forces required to give to the two particles the circular motions which have just been considered.

Now, what we have done for any one particle may be conceived of as done for all the particles in a wave. To understand the nature of a wave in this scheme, we must think of a series of particles originally in a straight line in the direction of propagation of the ray, as displaced to positions on a helix surrounding that direction. Fig. A

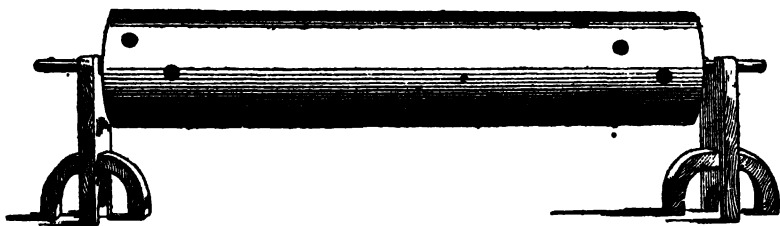


FIG. 11.

of this diagram (Fig. 10), regarded from the lower end, and the black spots on the model before you, show a left-handed helical arrangement. Let these particles be projected with equal speeds in the circular paths represented by the circle at the bottom of Fig. A. On this circle are seen the apparent positions of different particles in the helical arrangement when it is viewed by an eye looking upwards along its axis. This motion is shown by that of the black spots on the surface of the model (Fig. 11), when I set it into rotation about its axis. Let the particles be constrained to continue in motion exactly in this manner. As the model shows, the helical arrangement of the particles is displaced along the cylinder. This is the mode of propagation of a *circularly* polarised wave, which is made up of helical arrangements of particles which were formerly in straight lines parallel to the axis.

The direction of propagation of the wave is clearly from the bottom of the diagram to the top, and from the end of the model towards your left to the other, when the particles have a right-handed motion, and is in the contrary direction when the direction of rotation is reversed. For a right-handed helical arrangement the direction of

propagation for the same direction of motion of the particles is the opposite of that just specified. The direction of propagation remains therefore the same when the direction of motion and the helical arrangement of the particles are both reversed. All this can be made out from the diagram. Fig. B shows part of a right-handed arrangement of particles corresponding to the opposite arrangement of Fig. A; and if the particles have the motions shown at the bottom of the diagram, the propagation will be for both in the same direction from the bottom to the top.

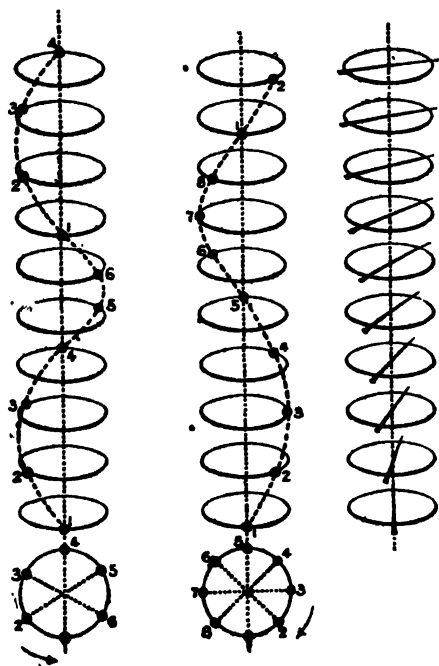


FIG. 12.

In Fig. 10 we suppose the periods equal and also the wave-lengths, the distance along the axis from particle 1 to particle 9. The combination of the circular motions A and B gives rectilinear motion; the combination of the wave motions of Figs. A and B gives a plane polarised wave, the plane of polarisation of which does not change in position. If, however, while the periods were equal, the wave-lengths were unequal, as shown in this other diagram (Fig. 12), the plane of polarisation would rotate, as shown by the lines drawn across the paths in the figure on the right, for the circular motions of particles in the longer wave would gain on those in the shorter.

A little consideration will show that the direction of the resultant rectilinear motion will, in consequence of the unequal speeds of propagation, turn round as the wave advances, and will do so in the direction of motion of the particles in the more quickly travelling wave, generating the screw surface shown in the model I have already exhibited.

We must now consider the forces. The particles moving in the circular paths have accelerations towards the centres of these paths, and forces must be applied to them to produce these accelerations. These forces are applied in the present theory by the action of the medium, and it is the reactions of the particles on the medium that are properly called the centrifugal forces of the particles. The requisite centreward forces then are supplied by the state of strain into which the medium is thrown by the displacement of parts of it, which form in the undisturbed position a series of straight arrays in the direction of propagation, into these helical arrangements round that direction. The greater these elastic forces the greater the velocity of propagation of the wave.

In an elastic medium these forces depend on the *amount* of the relative displacements of the particles, and will be greater for displacements in the right-hand helical arrangement than for displacements in the opposite direction if the medium has a greater rigidity for right-handed distortion than for left, and the right-handed wave of distortion will be transmitted with greater speed, and *vice versa*. This is the case of solutions of sugar and tartaric acid, quartz, &c., for which a helical structure has been supposed to exist in the medium.

Taking this case, refer to Figs. A and B of our large diagram (Fig. 10), and let the right-handed wave travel the faster. Let the waves travel up, be reflected at the upper ends, as at the surface of a denser medium, and then travel down again. The reflected waves are those shown in Figs. A', B' of the diagram. By the reflection the helical arrangement will be unaltered. But the plane of polarisation, as we have seen, turns round in space in the direction of the motion of the particles in the more quickly moving wave; it therefore turns round in the direction of the hands of a watch as the wave moves in the upward direction in the diagram, and in the opposite direction when the wave is travelling back. Thus the rotation of the plane of polarisation produced in the forward passage is undone in the backward.

It is easy to see that the same thing will take place if the reflection is at the surface of an optically rarer medium, so that the direction of motion of the particles is the same in the reflected as in the direct wave. The helical arrangements, however, are reversed by the reflection, and hence the wave which travelled the more quickly forward travels the more slowly back, and again the turning of the plane of polarisation is annulled by the backward passage. Thus Lord Kelvin's hypothesis of difference of structure completely explains the phenomena.

We pass now to the other case, that of magneto-optic rotation. Let us suppose, to fix the ideas, that the right-handed circular ray travels faster than the other, and that whether direct or reversed. Here, as in the other case, the elastic reaction of the medium on the displaced particles depends only on the distortion, and if there be no structural peculiarity in the medium there must be the same reaction in the particles in both the circular waves which combine to make up the plane polarised one.

Thus the actions on the particles being the same for both waves, and the velocities of propagation being different, the motions concerned in the light propagation cannot be the same. There must in fact be a motion already existing in the medium which, compounded with the motions concerned in light propagation, give two motions which give equal reactions in the medium against the equal elastic forces, applied to the particles in the case of equal helical displacements.

Thus Lord Kelvin supposes that in the medium in the magnetic field there exists a motion capable of being compounded with the luminiferous motion of either circularly polarised beam. The latter is thus only a component of the whole motion.

In the very important paper in which he has set forth his theory Lord Kelvin expresses his strong conviction that his dynamical explanation is the only possible one. If this view be correct, Faraday's magneto-optic discovery affords a demonstration of the reality of Ampère's theory of the ultimate nature of magnetism. For we have only to consider the particles of a magnetised body as electrons or groups of charges of electricity, ultimate as to smallness, rotating about axes on the whole in alignment along the direction of the magnetic force, and with a preponderance of one of the two directions of rotation over the other. Each rotating molecule is an infinitesimal electro-magnet, of which the current distribution is furnished by the system of convection currents constituted by the moving charges.

The subject of magneto-optic rotation has also been considered by Larmor, and two types of theory of these effects have been indicated by him in his report on the 'Action of Magnetism on Light.' One is represented by Lord Kelvin's theory, which is illustrated by Maxwell's chapter on molecular vortices in his 'Electricity and Magnetism.' FitzGerald's paper "On the Electromagnetic Theory of the Reflection and Refraction of Light," in the 'Philosophical Transactions' for 1880, is related to Maxwell's theory, and explains the rotation produced by reflection from the pole of a magnet by means of the addition of a term to the energy of the system. The other theory is also a purely electromagnetic one, and supposes that the effects are due to a kind of æolotropy of the medium set up by the magnetisation, and so attributes them to a change of structure which introduces rotational terms into the equations connecting *electric* displacements and electric forces. This latter theory therefore

regards the magneto-optic rotation as only a secondary effect of the magnetisation, which is not supposed to exert any direct dynamical influence on the transmission of the light-waves.

It is not possible here to enter into the subject of these theories, but I should like to direct attention to a paper by Mr. J. G. Leatham, just published in the 'Philosophical Transactions,' in which the type of theory just referred to has been worked out and compared in its results with the experiments of Sissingh and Zeeman in reflection. These investigators made measurements of the phase and amplitude of the magneto-optic component of the reflected light for various angles of incidence. For both these quantities the theoretical results of Leatham agree very well with the observed values.

Returning now to the gyrostatic medium, between which and the electro-magnetic theory, it is to be remembered, there is a correspondence, we may inquire in what way the gyrostat, when moved by the vibrations of the medium, react upon it, and so affect the velocity of propagation. The motion of a gyrostat is often regarded as mysterious, and it can hardly be fully explained except by mathematical investigation. But the general nature of its action may be made out without much difficulty. First of all, a gyrostat consists of a massive fly-wheel running on bearings attached to a case which more or less completely encloses the wheel. The mass of the wheel consists in the main of a massive rim, which renders as great as possible what is called the moment of momentum of the wheel when rotating about its axis. The diagram (Fig. 13) represents a partial section of the case and fly-wheel of a gyrostat, showing the arrangement of fly-wheel and bearings.

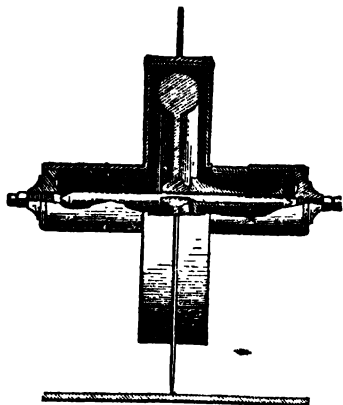


FIG. 13.

Now let the fly-wheel of such a gyrostat be rapidly rotated, and the gyrostat be hung up, as shown in this other diagram (Fig. 14), with the plane of the fly-wheel vertical, and a weight attached to one extremity of the axis. The gyrostat is not tilted over, but begins to turn round the cord by which it is suspended with a slow angular motion which is in the direction of the horizontal arrow if the direction of rotation is that of the circular arrow shown in the case. The same thing is shown by the experiment I now make. I spin this gyrostat, and hang it with the axis of rotation horizontal by passing a loop of cord round one end of the axis so that the weight of the gyrostat itself forms the weight tending to tilt it over about the point of suspension. The



axis of rotation here again remains nearly horizontal, but turns slowly round in a horizontal plane as before.

The explanation in general terms is this. The weight gives a couple tending to turn the gyrostat about a horizontal axis at right angles to that of rotation. This couple in any short interval of time produces moment of momentum about the axis specified, the amount of which is the moment of the couple multiplied by the time, and may be represented in direction and magnitude by the line  $OB$ . This must be compounded with the moment of momentum  $OA$  already existing about the axis of rotation, and gives for the resultant moment of momentum the line  $OC$ , which is the direction of the axis of rotation after the lapse of the short interval of time. The axis of rotation thus turns slowly round in the horizontal plane, and the more slowly the more rapidly the fly-wheel rotates.

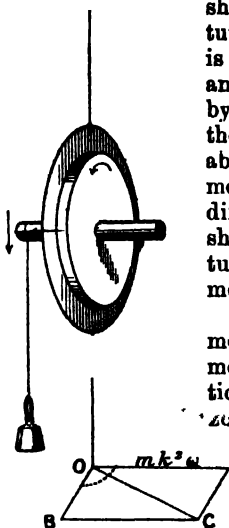


FIG. 14.

The gyrostat in fact must have this precessional motion, as it is sometimes called, in order that the moment of momentum of the gyrostat about a vertical axis may remain zero. That it must remain zero follows from the fact that there is no couple in a horizontal plane acting on the gyrostat.

Thus any couple tending to change the direction of the axis in any plane produces a turning in a perpendicular plane. For example, if a horizontal couple, that is about a vertical axis, were applied to the axis of the

gyrostat in the last figure it would turn about a horizontal axis, that is, would tilt over.

Again, consider a massive fly-wheel mounted on board ship on a horizontal axis in the direction across the ship. The rolling of the ship changes the direction of the axis, and produces a couple applied by the fly-wheel to the bearings, and an equal and opposite couple applied by the bearings to the fly-wheel. This couple is in the plane of the deck, and is reversed with the direction of rolling, and has its greatest value when the rate of turning of the ship is greatest. Thus the force on one bearing is towards the bow of the ship, the force on the other towards the stern, during a roll from one side to the other; and these forces are reversed during the roll back again. This is the gyrostatic couple exerted on its bearings by the armature of a dynamo on shipboard.

In the same way when a gyrostat is embedded in a medium and the medium is moving so as to change the direction of the axis of rotation, a couple acting on the medium in a plane at right angles to the plane of the direction of motion is brought into play. To fix the ideas, think of a row of small embedded gyrostats along this table, with their axes in the direction of the row, and their fly-wheels all rotating

in the same direction. Now let a wave of transverse displacement of the medium in the vertical direction pass along the medium in the direction of the chain. The vibratory motion of each part of the medium will turn the gyrostatic axis from the horizontal, and thereby introduce horizontal reactions on the medium. Again, a wave of horizontal vibratory motion will introduce vertical reactions in the medium from the gyrostats.

Now a wave of circular vibrations, like those we have already considered, passing through the medium in the direction of the chain, could be resolved into two waves of rectilinear vibration, one in which the vibration is horizontal, and another in which the vibration is vertical, giving respectively vertical and horizontal reactions in the medium. The magnetisation of the medium is regarded as due to the distribution throughout it of a multitude of rotating molecules, so small that the medium, notwithstanding their presence, seems of uniform quality. The molecules have, on the whole, an alignment of their axes in the direction of magnetisation. These reactions on the medium when worked out give terms in the equations of wave propagation of the proper kind to represent magneto-optic rotation.

It is worthy of mention that the addition of such terms to the equation was made by McCullagh, the well-known Irish mathematician, who, however, was unable to account for them by any physical theory. The necessary physical theory may be regarded as afforded by the mechanism which thus forms an essential part of Lord Kelvin's mode of accounting for magneto-optic effects.

Lord Kelvin, in his Baltimore Lectures, has suggested for magneto-optic rotation a form of gyrostatic molecule consisting, as shown in the figure, of a spherical sheath enclosing two equal gyrostats. These are connected with each other and with the case by ball-and-socket joints at the extremities of their axes, as shown in Fig. 15. If the spherical case were turned round any axis through the centre no disalignment of the gyrostats contained in it would take place, and it would act just like a simple gyrostat. If, however, the case were to undergo translation in any direction except along the axis, the gyrostats would lag behind, and the two-link chain which they form would bend at the centre. This bending would be resisted by the quasi-rigidity of the chain produced by the rotation, and the gyrostats would react on the sheath at the joints with forces as before at right angles to the plane in which the change of direction of the axis takes place.

The general result is, that if the centre of this molecule be carried with uniform velocity in a circle in a plane at right angles to the line

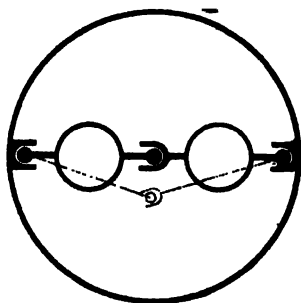


FIG. 15.

of axes, the force required for the acceleration towards the centre, and which is applied to it by the medium, is greater or less according as the direction in which the molecule is carried round is with or against the direction of rotation of the gyrostats. That is, the effect of the rotation is to virtually increase the inertia of the molecule in the one case and diminish it in the other.

These molecules embedded in the medium are supposed to be exceedingly small, and to be so distributed that the medium may, in the consideration of light propagation, be regarded as of uniform quality. Lord Kelvin's last form of molecule, it may be pointed out, if the surface of its sheath adheres to the medium, will have efficiency as an ordinary single gyrostat as regards rotations of the molecule,

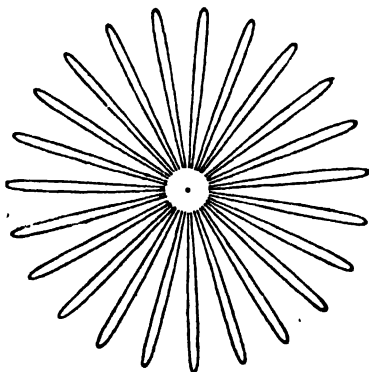


FIG. 16.—Path of the Bob of a Gyrostatic Pendulum.

As the pendulum moves, it passes from one ray to another on the opposite side, and the direction of motion at each swing alters through the angle between two rays. The central parts of the rays are left out. The marking point does not pass exactly through the centre.

and efficiency likewise as regards translational motion of the centre of the molecule. The former efficiency can be made as small as may be desired by making the molecule sufficiently small; the latter may be maintained at the same value under certain conditions, however small the molecule be made.

The lately discovered effect of a magnetic field in giving one period of circular oscillation of a particle or another according as the particle is revolving in one direction or the other about the direction of the magnetic force, is connected with magneto-optic rotation. There is a connection between velocity of propagation and frequency of vibration, which is exemplified by the phenomena of dispersion. In the Faraday effect, the two modes of vibration, if of the same period, have different velocities of vibration, consequently these two modes

of vibration must have different frequencies for the same velocity of propagation.

The vibrations of the molecules of a gas in which the Zeeman effect is produced by a magnetic field may be represented by the motion of a pendulum the bob of which contains a rapidly rotating gyrostat with its axis in the direction of the supporting wire of the pendulum. The period of revolution of the bob when moving as a conical pendulum is greater or less than the period when the gyrostat is not spinning according as the direction of revolution is against or with the direction of rotation.

The bob when deflected and let go moves in a path which constantly changes its direction, so that if a point attached to the bob writes the path on a piece of paper, a star-shaped figure is obtained. I cause the gyrostatic pendulum here suspended to draw its path by a stream of white sand on the blackboard placed below it, and you see the result.

I must here leave the subject, and may venture to express the hope that on some other occasion some one more specially acquainted with the electromagnetic aspects of the phenomenon may be induced to place the latest results of that theory before you.

[A. G.]

Friday, May 13, 1898.

LUDWIG MOND, Esq. Ph.D. F.R.S. Vice-President, in the Chair.

PROFESSOR W. A. TILDEN, D.Sc. F.R.S.

*Recent Experiments on Certain of the Chemical Elements  
in relation to Heat.*

THE discovery that different substances have different capacities for heat is usually attributed to Irvine, but there can be no doubt that Black, Crawford and others contributed to the establishment of the idea. The fact that equal weights of different substances, in cooling down through the same number of degrees, give out different amounts of heat, may be illustrated by the well-known experiment, in which a cake of wax is penetrated with different degrees of rapidity by balls of different metals heated to the same temperature. But, for the quantitative estimation of the amounts of heat thus taken up and given out again—that is, the *specific heats*—the physicist must resort to other forms of experiment, each of which presents difficulties of its own. Broadly speaking, three principal methods have been used in the past for this purpose. The first is based upon the observation of the exact change of temperature produced in a known mass of water, by mixing with it a known weight of the substance previously, at a definite temperature above or below that of the water. The second consists in determining the quantity of ice melted, when the heated body is brought into contact with it in such a way that no heat from any other source can reach the ice. And the third method consists in observing the rate at which the temperature of the heated body falls through a definite range of degrees, when suspended in a vacuous space, as compared with the rate of cooling of another body taken as the standard.

The process of intermixture with water was used by the earlier experimenters in the last century, and some of the best results extant have been obtained by this method, which, however, is not so easy as it appears when the highest degree of accuracy is desired.

Lavoisier and Laplace, in 1780, devised the ice calorimeter which bears their name; and in a most interesting memoir, which is reprinted among Lavoisier's works, they show that they were familiar with the idea which in modern times is expressed as the principle of the conservation of energy. In this memoir they give the results of experiments, in which the specific heats of iron, mercury and a

few other substances are estimated with a very tolerable approach to accuracy. Although many of the metals were known to them, and supposing they had persisted in this work, it would not have been possible for them to make the discovery which was reserved for Dulong and Petit thirty-five years later, for the atomic theory had not then been conceived, and no elemental combining proportions had been determined.

Dulong and Petit \* seem to have used at first the method of mixtures, and to have found, by direct experiment, that the specific heat of solids (metals and glass) increases with the temperature. They also studied (after Leslio) the laws of cooling of bodies; and two years after the publication of their first paper on the subject, they (Petit and Dulong, *sic*) arrived at the remarkable general expression which is associated with their names.†

After pointing out that all the results of previous experiments except those of Lavoisier and Laplace are extremely incorrect, they describe their own conclusions obtained by the method of cooling, conducted with many precautions to avoid error. The numerical expression of their experimental results is given in the following table:—

COPY OF TABLE BY PETIT AND DULONG.  
(Ann. Chim. Phys. 1819, x. 403.)

—	Specific Heats.	Atomic Weights ( $0 = 1$ ).	Atomic Weight × Specific Heat.
Bismuth .. .. .	·0288	13·30	·3830
Lead .. .. .	·0293	12·95	·3794
Gold .. .. .	·0298	12·43	·3704
Platinum .. .. .	·0314	11·16	·3740
Tin .. .. .	·0514	7·85	·3779
Silver .. .. .	·0557	6·75	·3759
Zinc .. .. .	·0927	4·03	·3736
Tellurium .. .. .	·0912	4·03	·3675
Copper .. .. .	·0949	3·957	·3755
Nickel .. .. .	·1035	3·69	·3819
Iron .. .. .	·1100	3·392	·3731
Cobalt .. .. .	·1498	2·46	·3685
Sulphur .. .. .	·1880	2·011	·3780

The statement of the relation indicated in the last column of figures is expressed in the following words of the authors, p. 405: "Les atomes de tous les corps simples ont exactement la même capacité pour la chaleur."

Here the question rested, till resumed many years later (1840) by Regnault, who in his first memoir ‡ pointed out the difficulties which

\* Ann. Chim. 1817, vii. 144.

† Ibid. 1819, x. 395.

‡ Ibid. 73/5.

attend the acceptance of the statement of Petit and Dulong in the form in which they gave it. He then discussed the three principal experimental methods: viz. (1) fusion of ice; (2) mixture with water or other liquid; and (3) cooling; and decided in favour of the second, which he used throughout his researches. The general form of the apparatus used by the great physicist has been a model for the guidance of successive experimentalists since his time.

Another quarter of a century elapsed before the question of the specific heats of the elements was resumed by Hermann Kopp. His results were communicated to the Royal Society, and are embodied in a paper printed in the 'Philosophical Transactions' for 1865. After reviewing the work of his predecessors, he described a process by which he had made a large number of estimations of specific heat, not only of elements, but of compounds of all kinds in the solid state. Concerning his own process, however, he remarks that "The method, as I have used it, has by no means the accuracy of that of Regnault" (p. 84).

In 1870 Bunsen introduced his well-known ice calorimeter. This is an instrument in which the amount of ice melted by the heated body is not measured by collecting and weighing the water formed, but by observing the contraction consequent upon the change of state. The results obtained by Bunsen himself are uniformly slightly lower than those of Regnault for the same elements.

Since that time, experiments have been made by Weber, Dewar, Humpidge and others, in connection especially with the influence of temperature in particular cases.

Setting aside the elements, carbon, boron, silicon and beryllium, as providing an entirely separate problem, the question is whether the law of Dulong and Petit is strictly valid when applied to the metals. Kopp, in the discussion of his subject, came to the conclusion that it is not; but the grounds for this conclusion are unsatisfactory, since neither the atomic weights nor the specific heats were at that time known with sufficient accuracy. It has been customary to assume that the divergences from the constant value of the product,  $\text{At. Wt.} \times \text{Sp. Ht.}$ , are due partly to the fact that at the temperature at which specific heats are usually determined, the different elements stand in very different relations to their point of fusion: thus, lead at the temperature of boiling water is much nearer to its melting point than iron under the same conditions. The divergences have also been attributed to temporary or allotropic conditions of the elements. As to the relation to melting point, the specific heats of atomic weights seem to be practically the same in separate metals and alloys of the same which melt at far lower temperatures. For example, the atomic heat of cadmium is 6.35; of bismuth 6.47; of tin, 6.63; and of lead, 6.50; while the mean atomic heat in alloys of bismuth with tin and lead with tin ranges from 6.40 to 6.66 (Regnault), which is practically the same. Again, while the melting point of platinum is at a white heat, the metal becomes plastic at a low red heat, and yet the

specific heat at this lower temperature is very little less than it is near the melting point. The properties of many other metals, notably zinc and copper, change considerably at temperatures far removed from their melting points without substantial change in their capacity for heat.

As to allotropy, it is a phenomenon which is comparatively rare among metals, and in the marked cases in which it occurs we have no information as to the value of the specific heats in the several varieties, such as the two forms of antimony and the silver-zinc alloy of Heycock and Neville, and they may be left out of account. Bunsen compared the so-called allotropic tin, obtained by exposing the metal to cold for a long time, and found it  $\cdot 0545$  against  $\cdot 0559$  for the ordinary kind.\* In dimorphous substances there is often no difference. Regnault found for arragonite  $\cdot 2086$  and for calcite  $\cdot 2085$  respectively. The differences between metals hammered and annealed, hard and soft, were also found by Regnault to be very small. †

Hard steel	$\cdot 1175$ .	Same, softened	$\cdot 1165$
Hard bronze	$\cdot 0858$ .	Same, softened	$\cdot 0862$

Kopp came to the conclusion, *first*, that each element in the solid state, and at a sufficient distance from its melting point, has *one* specific or atomic heat, which varies only slightly with physical conditions; and *secondly*, that each element has essentially the same specific or atomic heat in compounds as it has in the free state. This last is practically identical with the statement which is known as Neumann's law. With Kopp's conclusion I agree, but, from some of Regnault's results coupled with my own, the effect of *small* quantities of carbon and perhaps of sulphur upon the specific heats of metals is greater than has been supposed. If we take the results of Regnault and of Kopp and combine them with the most accurately known atomic weights, the products are still not constant.

ATOMIC WEIGHTS MOST ACCURATELY KNOWN (1897) COMBINED  
WITH SPECIFIC HEATS.

	A.W. (H=1).	S. H. Regnault.	S. H. Kopp.	At. Ht. Regnault.	At. Ht. Kopp.
Copper .. .. .	63.12	$\cdot 09515$	$\cdot 0930$	6.01	5.87
Gold .. .. .	195.74	$\cdot 03244$	..	6.35	..
Iron .. .. .	55.60	$\cdot 11379$	$\cdot 1120$	6.33	6.23
Lead .. .. .	205.36	$\cdot 03140$	$\cdot 0315$	6.45	6.47
Mercury liq. .. .. .	198.49	$\cdot 03332$	..	6.61	..
„ - 78° to + 10° sol.	198.49	$\cdot 03192$	..	6.34	..
Silver .. .. .	107.11	$\cdot 05701$	$\cdot 0560$	6.11	6.00
Iodine .. .. .	125.89	$\cdot 05412$	..	6.81	..



The "Law" of Dulong and Petit is therefore only an approximation; but this may perhaps be due to inaccuracy in the estimation of the specific heat, owing to impurity in the material used. That is the problem which I have endeavoured to solve.

The introduction by Professor J. Joly of a new method of calorimetry, which depends upon the condensation of steam upon the cold body, and the excellent results obtained by the Author in the use of the differential form of his instrument,\* led me to think that with due attention to various precautions—such as exact observations of the temperatures, and practice in determining the moment at which the increase of weight due to condensation is completed—results of considerable accuracy might be obtained.

The problem is to find two elements, very closely similar in density and melting point, which can be obtained in a state of purity, and then to determine with the utmost possible accuracy the specific heat of each under the same conditions.

The two metals cobalt and nickel were selected for the purpose. They were examined by Regnault, but the metals he used were very impure.

The cobalt employed in my experiments was prepared by myself. For the nickel I am indebted to Dr. Ludwig Mond. Both were undoubtedly much more nearly pure than any metal available in Regnault's time. The results obtained are as follows:—

#### SPECIFIC HEATS OF COBALT AND NICKEL.

*Pure fused.*

Cobalt, S. G. $\frac{21^{\circ}}{45}$ , 8.718.	Nickel, S. G. $\frac{21^{\circ}}{45}$ 8.790.
·10310	
·10378	
·10310	·10953
·10355	·10910 } too high?
·10373	·10930
·10362	
th. mean .. .. 10348	·10931

The value arrived at for cobalt is much lower than that (·1067) derived from Regnault's experiments, while that for nickel is practically identical with Regnault's, which is ·1092. This is certainly too high.

Further experiments will be made. Already, however, I feel certain that Kopp's conclusion is right, and that the law of Dulong and Petit, even for the metals, is an approximation only, and

\* Proc. R. S. 47, 241.

cannot be properly expressed in the words of the discoverers. For, although the exact values of the atomic weights of these two elements, cobalt and nickel, are not known, it is certain that they are not so far apart as would be implied by these values for the specific heats.

Two other examples of somewhat similar kind are shown by gold and platinum, copper and iron.

For the gold I naturally applied to my colleague, Professor Roberts-Austen. The platinum I prepared from ordinary foil, by resolution and re-precipitation as ammonio-chloride, and subsequent heating. Both metals were fused into buttons before use. The atomic heats come closer together than those of Co and Ni.

Copper and iron differ considerably in melting point, but both at the temperature of  $100^{\circ}$  are far removed from even incipient fusion. The copper was prepared from pure sulphate by electrolysis, the iron by reduction of pure oxide in pure hydrogen. Notwithstanding all our care, it was disappointing to find it contained .01 per cent. of carbon, the source of which I am at a loss to explain. This iron is purer than any examined by Regnault or Kopp.

#### SPECIFIC HEATS OF GOLD AND PLATINUM.

##### *Pure fused.*

Gold, S. G.	$18^{\circ}$ $18^{\circ}$	19.227.		Platinum, S. G.	$18^{\circ}$ $18^{\circ}$	21.323
		.03052				.03147
		.03017				.03150
		.03035				.03144
Arith. mean	.. ..	.03035		Arith. mean	.. ..	.03147
Atomic heat	.. ..	5.94		Atomic heat	.. ..	6.05

#### SPECIFIC HEATS OF COPPER AND IRON.

##### *Fused.*

Copper (pure) S. G.	$20^{\circ}$ $20^{\circ}$	8.522.		Iron, S. G.	$15^{\circ}$ $15^{\circ}$	7.745, contains 0.01 per cent. copper.
		.09248				.11022
		.09241				.11037
		.09205				
		.09234				
Arith. mean	.. ..	.09232		Arith. mean	.. ..	.11030
Atomic heat	.. ..	5.83		Atomic heat	.. ..	6.13

The differences observed between cobalt and nickel, and between gold and platinum, are manifestly not due to allotropes or to differ-

ences of melting point, which in these cases can have no effect on the result: So large a difference must be due to peculiarities inherent in the atoms themselves; and differences of atomic heat are to a certain extent comparable with the differences observed in other physical properties, which, like specific volume, specific refraction, &c., are approximately additive.

If we try to think what is going on in the interior of a mass of solid when it is heated, the work done is expended not only in setting the atoms into that kind of vibration which corresponds to rise of temperature, that is, it makes them hotter, but partly in separating the molecules or physical units from one another (= expansion) and partly in doing *internal* work of some kind, the nature of which is not known. A difference between metals and non-metals has been brought out by the researches of Heycock and Neville, who find that metals dissolved in metals are generally monatomic; whereas it is generally admitted that iodine, sulphur and phosphorus in solution are polyatomic. It is moreover remarkable that, although in respect to specific heat each element in a solid seems to be independent of the other elements with which it is associated, when the elementary substances are vaporised some rise in separate atoms like mercury, some in groups of atoms-like iodine, sulphur, arsenic and phosphorus, and as the temperature is raised these groups are simplified with very varying degrees of readiness.

The two metals, cobalt and nickel, with which I began my inquiry, have very nearly the same atomic weight, the value,  $58.24$  for nickel and that for cobalt  $58.49$ , being calculated by F. W. Clarke from the results of a great many analyses by many different chemists. They are so close together that for a long time they were regarded as identical, and Mendeléef does not hesitate even to invert the order by making  $\text{Co} = 58.5$  and  $\text{Ni} = 59$ . These metals, nevertheless, differ from each other in several very important chemical characters. Nickel, for example, forms the well known and highly remarkable compound with carbonic oxide discovered by Dr. Mond. Cobalt, on the other hand, produces many ammino-compounds to which there is nothing corresponding among the compounds of nickel.

Having put aside the common excuses for the observed divergences from the constant of Dulong and Petit, we are compelled to look round for some other hypothesis to explain them.

The constitution of carbon compounds is now accounted for by a hypothesis concerning the configuration of the carbon atom introduced by Van't Hoff and Le Bel twenty-five years ago, and which is now accepted by the whole chemical world. It seems not unreasonable to apply a similar idea to the explanation of those cases of isomerism which have been observed in certain compounds of the metals, notably chromium, cobalt and platinum. This has already been done by Professor Werner, of Zürich. If the constitution of compounds can be safely explained by such hypothesis, this implies the assumption of peculiarities in the configuration of the individual constituent metals

around which the various radicles are grouped in such compounds ; and hence peculiarities in the behaviour of such metals in the elemental form may possibly be accounted for. For the atom of cobalt Professor Werner employs the figure of the regular octahedron. For nickel, therefore, which differs from cobalt in many ways, a different figure must be chosen. This, however, is for the present a matter of pure speculation.

W. A. T.

Friday, June 10, 1898.

SIR WILLIAM HUGGINS, K.C.B. D.C.L. LL.D. F.R.S. Vice-President,  
in the Chair.

The Right Hon. LORD RAYLEIGH, M.A. D.C.L. LL.D. F.R.S. *M.R.I.*  
Professor of Natural Philosophy, *R.I.*

*Some Experiments with the Telephone.*

EARLY estimates of the minimum current of suitable frequency audible in the telephone having led to results difficult of reconciliation with the theory of the instrument, experiments were undertaken to clear up the question. The currents were induced in a coil of known construction, either by a revolving magnet of known magnetic moment, or by a magnetised tuning-fork vibrating through a measured arc. The connection with the telephone was completed through a resistance which was gradually increased until the residual current was but just easily audible. For a frequency of 512 the current was found to be  $7 \times 10^{-8}$  ampères.\* This is a much less degree of sensitiveness than was claimed by the earlier observers, but it is more in harmony with what might be expected upon theoretical grounds.

In order to illustrate before an audience these and other experiments requiring the use of a telephone, a combination of that instrument with a sensitive flame was introduced. The gas, at a pressure less than that of the ordinary supply, issues from a pin-hole burner† into a cavity from which air is excluded (see figure). Above the cavity, and immediately over the burner, is mounted a brass tube, somewhat contracted at the top where ignition first occurs.‡ In this arrangement the flame is in strictness only an indicator, the really sensitive organ being the jet of gas moving within the cavity and surrounded by a similar atmosphere. When the pressure is not too high, and the jet is protected from sound, the flame is rather tall and burns bluish. Under the influence of sound of suitable pitch the jet is dispersed. At first the flame falls,

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\* The details are given in 'Phil. Mag.' vol. xxxviii. p. 285 (1894).

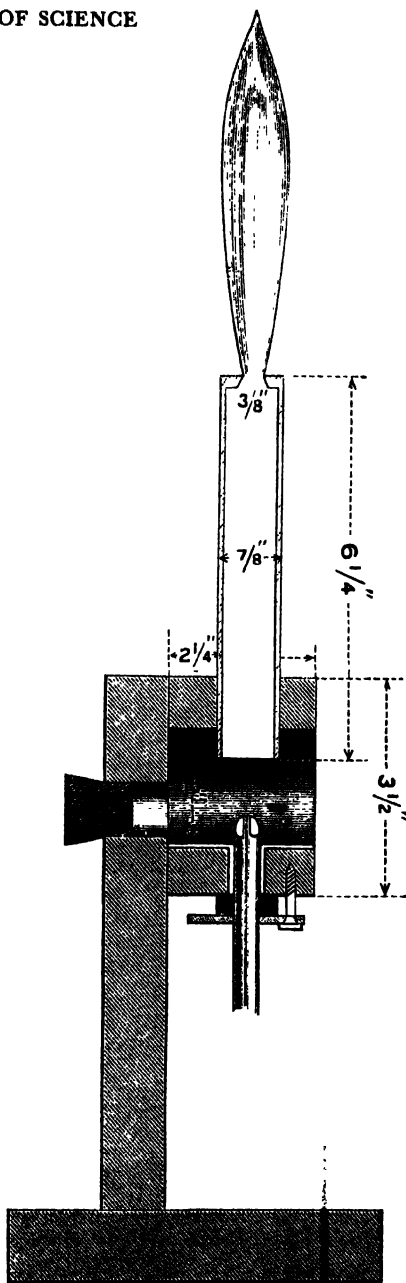
† The diameter of the pin-hole may be 0.03".

‡ 'Camb. Proc.' vol. iv. p. 17, 1880.

becoming for a moment almost invisible; afterwards it assumes a more smoky and luminous appearance, easily distinguishable from the unexcited flame.

When the sounds to be observed come through the air, they find access by a diaphragm of tissue paper with which the cavity is faced. This serves to admit vibration while sufficiently excluding air. To get the best results the gas pressure must be steady, and be carefully adjusted to the maximum (about 1 inch) at which the flame remains undisturbed. A hiss from the mouth then brings about the transformation, while a clap of the hands or the sudden crackling of a piece of paper often causes extinction, especially soon after the flame has been lighted.

When the vibrations to be indicated are electrical, the telephone takes the place of the disc of tissue paper, and it is advantageous to lead a short tube from the aperture of the telephone into closer proximity with the burner. The earlier trials of the combination were comparative failures, from a cause that could not at first be traced. As applied, for instance, to a Hughes' induction balance, the apparatus failed to indicate with certainty the introduction of a *shilling* into one of the cups, and the performance, such as it was, seemed to deteriorate after a few minutes' experimenting. At this stage an observation was made which ultimately afforded a clue to the anomalous behaviour. It was found that the telephone became dewed. At first it seemed incredible that this could come from



the water of combustion, seeing that the lowest part of the flame was many inches higher. But desiccation of the gas on its way to the nozzle was no remedy, and it was soon afterwards observed that no dewing ensued if the flame were all the while under excitation, either from excess of pressure or from the action of sound. The dewing was thus connected with the *unexcited* condition. Eventually it appeared that the flame in this condition, though apparently filling up the aperture from which it issues, was nevertheless surrounded by a descending current of air carrying with it part of the moisture of combustion. The deposition of dew upon the nozzle was thus presumably the source of the trouble, and a remedy was found in keeping the nozzle warm by means of a stout copper wire (not shown) conducting heat downwards from the hot tube above.

The existence of the downward current could be made evident to private observation in various ways, perhaps most easily by projecting little scraps of tinder into the flame, whereupon bright sparks were seen to pass rapidly downwards. In this form the experiment could not be shown to an audience, but the matter was illustrated with the aid of a very delicate ether manometer devised by Professor Dewar. This was connected with the upper part of the brass tube by means of a small lateral perforation just below the root of the flame. The influence of sound and consequent passage of the flame from the unexcited to the excited condition was readily shown by the manometer, the pressure indicated being less in the former state of things.

The downward current is evidently closely associated with the change of appearance presented by the flame. In the excited state the gas issues at the large aperture above as from a reservoir at very low pressure. The unexcited flame rises higher, and must issue at a greater speed, carrying with it not only the material supplied from the nozzle, and constituting the original jet, but also some of the gaseous atmosphere in the cavity surrounding it. The downward draught thus appears necessary in order to equalise the total issue from the upper aperture in the two cases.

Although the flame falls behind the ear in delicacy, the combination is sufficiently sensitive to allow of the exhibition of a great variety of interesting experiments. In the lecture the introduction of a threepenny piece into one of the cups of a Hughes' induction balance was made evident, the source of current being three Leclanché cells, and the interrupter being of the scraping contact type actuated by clockwork.

Among other experiments was shown one to prove that in certain cases the parts into which a rapidly alternating electric current is divided may be greater than the whole.\* The divided circuit was formed from the three wires with which, side by side, a large flat

\* See 'Phil. Mag' vol. xxii. p. 496 (1886).

coil is wound. One branch is formed by two of these wires connected in series, the other (in parallel with the first), by the third wire. Steady currents would traverse all three wires in the same direction. But the rapidly periodic currents from the interrupter distribute themselves so as to make the self-induction, and consequently the magnetic field, a minimum; and this is effected by the assumption of opposite values in the two branches, the ratio of currents being as 2 : - 1. On the same scale the total or main current is + 1. It was shown by means of the telephone and flame that the current in one branch was about the same (arithmetically) as in the main, and that the current in the other branch was much greater. [R.]



Friday, January 20, 1899.

SIR FREDERICK BRAMWELL, BART., D.C.L. LL.D. F.R.S., Honorary  
Secretary and Vice-President, in the Chair.

PROFESSOR DEWAR, M.A. LL.D. F.R.S. M.R.I.

### *Liquid Hydrogen.*

FROM the year 1878, when the experiments of Cailletet and Pictet were attracting the attention of the scientific world, it became a common habit in text-books to speak of all the permanent gases, without any qualification, as having been liquefied, whereas these experimentalists, by the production of an instantaneous mist in a glass tube of small bore, or a transitory liquid jet in a gas expanding under high compression into air, had only adduced evidence that sooner or later the static liquid form of all the known gases would be attained. Neither Pictet or Cailletet in their experiments ever succeeded in collecting any of the permanent gases in that liquid form for scientific examination. Yet we meet continually in scientific literature with expressions which lead one to believe that they did. For instance, the following extract from the 'Proceedings' of the Royal Society, 1878, illustrates this point very well: "This award (Davy Medal) is made to these distinguished men (Cailletet and Pictet) for having independently and contemporaneously liquefied the whole of the gases hitherto called permanent." Many other quotations of the same kind may be made. As a matter of fact six years elapsed, during which active investigation in this department was being prosecuted, before Wroblewski and Olszewski succeeded in obtaining oxygen as a static liquid, and to collect liquid hydrogen, which is a much more difficult problem, has taken just twenty years from the date of the Pictet and Cailletet experiments.

Wroblewski made the first conclusive experiment on the liquefaction of hydrogen in January 1884. He found that the gas cooled in a capillary glass tube to the boiling point of oxygen, and expanded quickly from 100 to 1 atmosphere, showed the same appearance of sudden ebullition lasting for a fraction of a second, as Cailletet had seen in his early oxygen experiments. No sooner had the announcement been made, than Olszewski confirmed the result by expanding hydrogen from 190 atmospheres, previously cooled to the temperature given by liquid oxygen and nitrogen evaporating under diminished pressure. Olszewski, however, declared in 1884 that he saw colourless

drops, and by partial expansion to 40 atmospheres, the liquid hydrogen was seen by him running down the tube. Wroblewski could not confirm Olszewski's results, his hydrogen being always obtained in the form of what he called a "liquide dynamique," or the appearance of an instantaneous froth. Olszewski himself seven years later repeated his experiments of 1884 on a larger scale, confirming Wroblewski's results, thereby proving that the so-called liquid hydrogen of the earlier experiments must have been due to some impurity. The following extract from Wroblewski's paper states very clearly the results of his work on Hydrogen:—

"L'hydrogène soumis à la pression de 180 atm. jusqu'à 190 atm., refroidi par l'azote bouillant dans la vide (à la température de sa solidification) et détendu brusquement sous la pression atmosphérique présente une mousse bien visible. De la couleur grise de cette mousse, où l'œil ne peut distinguer des gouttelettes incolores, on ne peut pas encore deviner quelle apparence aurait l'hydrogène à l'état de liquide statique et l'on est encore moins autorisé à préciser s'il a ou non une apparence métallique. J'ai pu placer dans cette mousse ma pile thermo-électrique, et j'ai obtenu suivant les pressions employées des températures de  $-208^{\circ}$  jusqu'à  $-211^{\circ}$  C. Je ne peux pas encore dire dans quelle relation se trouvent ces nombres avec la température réelle de la mousse ou avec la température d'ébullition de l'hydrogène sous la pression atmosphérique, puisque je n'ai pas encore la certitude que la faible durée de ce phénomène ait permis à la pile de se refroidir complètement. Néanmoins, je crois aujourd'hui de mon devoir de publier ces résultats, afin de préciser l'état actuel de la question de la liquéfaction de l'hydrogène." \*

It is well to note that the lowest thermo-electric temperature recorded by Wroblewski during the adiabatic expansion of the hydrogen (namely,  $-211^{\circ}$ ) is really equivalent to a much lower temperature on the gas-thermometer scale. The most probable value is  $-230^{\circ}$ , and this must be regarded as the highest temperature of the liquid state, or the critical point of hydrogen, according to his observations. In a posthumous paper of Wroblewski's on 'The Compression of Hydrogen,' published in 1889, an account appears of further attempts which he had made to liquefy hydrogen. The gas compressed to 110 atmospheres, was cooled by means of liquid nitrogen under exhaustion to  $-213.8^{\circ}$ . By suddenly reducing the pressure, as low a temperature as  $-223^{\circ}$  on his scale was recorded, but without any signs of liquefaction. This expansion gives a theoretical temperature of about  $15^{\circ}$  absolute in the gas particles. The above methods having failed to produce static hydrogen, Wroblewski suggested that the result might be attained by the use of hydrogen gas as a cooling agent. From this time until his death in the year 1888, Wroblewski devoted his time to a laborious research on the iso-

thermals of hydrogen at low temperatures. The data thus arrived at enabled him, by the use of Van der Waal's formulæ, to calculate the critical constants, and also the boiling point of liquid hydrogen.

Olszewski returned to the subject in 1891, repeating and correcting his old experiments of 1884, which Wroblewski had failed to confirm, using now a glass tube 7 mm. in diameter instead of one of 2 mm. as in the early trials. He says: "On repeating my former experiments, I had no hope of obtaining a lower temperature by means of any cooling agent, but I hoped that the expansion of hydrogen would be more efficacious, on account of the larger scale on which the experiments were made." The results of these experiments Olszewski describes as follows: "The phenomenon of hydrogen ebullition, which was then observed, was much more marked and much longer than during my former investigations in the same direction. But even then I could not perceive any meniscus of liquid hydrogen." Further, "*The reason for which it has not hitherto been possible to liquefy hydrogen in a static state, is that there exists no gas having a density between those of hydrogen and of nitrogen, and which might be for instance 7-10 ( $H = 1$ ). Such a gas could be liquefied by means of liquid oxygen or air as cooling agent, and be afterwards used as a frigorific menstruum in the liquefaction of hydrogen.*"

Professor Olszewski, in 1895, determined the temperature reached in the momentary adiabatic expansion of hydrogen at low temperatures, just as Wroblewski had done in 1885, only he employed a platinum-resistance thermometer instead of a thermo-junction. For this purpose he used a small steel bottle of 20 or 30 cc. capacity, containing a platinum-resistance thermometer; in this way, the temperatures registered were regarded as those of the critical and boiling points of liquid hydrogen, a substance which could not be seen under the circumstances and was only assumed to exist for a second or two during the expansion of the gaseous hydrogen in the small steel bottle.

The results arrived at by Wroblewski and Olszewski are given in the following table, and it will be shown later on that Wroblewski's constants are nearest the truth.

		Wroblewski, 1885.	Olszewski, 1895.
Critical temperature	.. .. .	-240°	-234°
Boiling point	.. .. .	-250°	-243°
Critical pressure	.. .. .	13 atm.	20 atm.

The accuracy of Wroblewski's deductions regarding the chief constants of liquid hydrogen following from a study of the isothermals of the gas is a signal triumph for the theory of Van der Waals and a monument to the genius of the Cracow physicist. From these results we may safely infer that supposing a gas is hereafter discovered in small quantity four times more volatile than liquid hydrogen, having a boiling point of about 5° absolute, and

therefore incapable of direct liquefaction by the use of liquid hydrogen, yet by a study of its isothermals we shall succeed in finding out its most important liquid constants, although the isolation of the real liquid may for the time be impossible.

In a paper published in the 'Philosophical Magazine,' September 1884, "On the Liquefaction of Oxygen and the Critical Volumes of Fluids," the suggestion was made that the critical pressure of hydrogen was wrong, and that instead of being 99 atmospheres (as deduced by Sarrau from Amagat's isothermals) the gas had probably an abnormally low value for this constant. This view was substantially confirmed by Wroblewski finding the critical pressure of 13.3 atmospheres, or about one-fourth of that of oxygen. The 'Chemical News,' September 7, 1894, contains an account of the stage the author's hydrogen experiments had reached at that date. The object was to collect liquid hydrogen at its boiling point, in an open vacuum vessel, which is a much more difficult problem than seeing it in a glass tube under pressure and at a higher temperature. In order to raise the critical point of hydrogen to about  $-210^{\circ}$ , from 2 to 5 per cent. of nitrogen or air was mixed with it. *This is simply making an artificial gas containing a large proportion of hydrogen which is capable of liquefaction by the use of liquid air.* The results are summed up in the following extract from the paper: "One thing can, however, be proved by the use of the gaseous mixture of hydrogen and nitrogen, namely that by subjecting it to a high compression at a temperature of  $-200^{\circ}$  and expanding the resulting liquid into air, a much lower temperature than anything that has been recorded up to the present time can be reached. This is proved by the fact that such a mixed gas gives, under the conditions, a paste or jelly of solid nitrogen, evidently giving off hydrogen, because the gas coming off burns fiercely. Even when hydrogen containing only some 2 to 5 per cent. of air is similarly treated, the result is a white solid matter (solid air) along with a clear liquid of low density, which is so exceedingly volatile that no known device for collecting it has been successful." This was in all probability the first liquid hydrogen obtained, and the method is applicable to other difficultly liquefiable gases.

Continuing the investigations during the winter of 1894, and the greater part of 1895, the author read a paper before the Chemical Society in December of that year entitled, "The Liquefaction of Air and Research at Low Temperatures," \* in which occasion was taken to describe for the first time the mode of production and use of a Liquid Hydrogen Jet. At the same meeting Professor William Ramsay made an announcement of a sensational character, which amounted to stating that my hydrogen results had been not only anticipated but bettered. The statement made to the Society by Professor Ramsay, read as

\* 'Proceedings' of the Chemical Society, No. 158, 1895.

follows: "*Professor Olszewski had succeeded in liquefying hydrogen, and from unpublished information received from Cracow, he (Ramsay) was able to state that a fair amount of liquid had been obtained, not as a froth, but in a state of quiet ebullition, by surrounding a tube containing compressed hydrogen by another tube also containing compressed hydrogen at the temperature of oxygen boiling at a very low pressure. On allowing the hydrogen in the middle jacket suddenly to expand, the hydrogen in the innermost tube liquefied, and was seen to have a meniscus. Its critical point and its boiling point, under atmospheric pressure, were determined by means of a resistance thermometer.*"\*

This announcement of Professor Ramsay's had from its very specific and detailed experimental character the merit of the appearance of being genuine, although it was never substantiated, either by the production of the Cracow document, or by any subsequent publication of such important results by Professor Olszewski himself. My observation at the time on Professor Ramsay's communication was that quotations had been made in my paper from the most recent publications of Professor Olszewski in which he made no mention of getting "*Static Hydrogen or of seeing a meniscus*" or of getting as Professor Ramsay alleged "*a fair amount of liquid, not as a froth, but in a state of quiet ebullition.*" To achieve such a result would require a very different scale of experiment from anything Professor Olszewski had so far described. Naturally an early corroboration of the startling statement made by Professor Ramsay as to this alleged anticipation was expected, but strange to say Professor Olszewski published no confirmation of the experiments detailed by Professor Ramsay in scientific journals of date immediately preceding my paper or during the following years 1896, 1897 or up to May 1898. The moment the announcement was made by me to the Royal Society in May 1898 that, after years of labour, hydrogen had at last been obtained as a static liquid, Professor Ramsay repeated the story to the Royal Society that Olszewski had anticipated my results (basing the assertion solely on the contents of the old letter received some two and a half years before), in spite of the fact that during the interval he, Professor Ramsay, must have known that Professor Olszewski had never corroborated in any publication either the form of the experiments he had so minutely described or the results which were said to follow. Challenged by me at the Royal Society Meeting on May 12, 1898, to produce Olszewski's letter of 1895, he did not do so, but at the next meeting of the Society, Professor Ramsay read a letter he had received during the interval from Professor Olszewski, denying that he had ever stated that he had succeeded in producing static liquid hydrogen. This oral communication of the contents of the new Olszewski letter (of which it is to be regretted there is no record in the published proceedings of the Royal Society) is the only kind of retraction Professor Ramsay has thought fit to make of his

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\* 'Proceedings' of the Chemical Society, No. 195, 1897-1898.

published mis-statements of fact. No satisfactory explanation has yet been given by Professor Ramsay of his twice-repeated categorical statements made before scientific bodies of the results of experiments which, in fact, had never been made by their alleged author. The publicity that has been given to this controversy makes it imperative that the matter should not be passed over, but once for all recorded.

The report of a Friday Evening Discourse on "New Researches on Liquid Air" \* contains a drawing of the apparatus employed

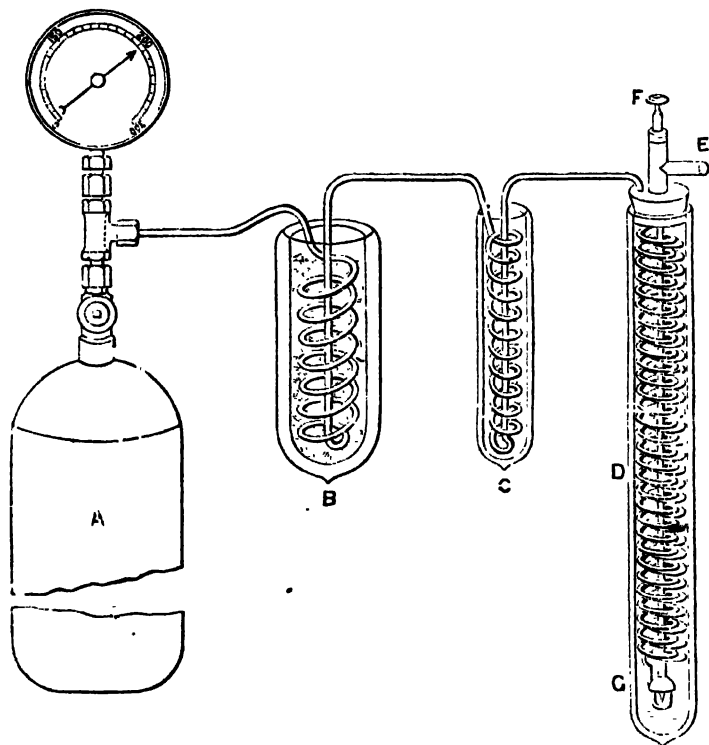


FIG. 1.

for the production of a jet of hydrogen containing visible liquid. This is reproduced in Fig. 1. A represents one of the hydrogen cylinders; B and C, vacuum vessels containing carbonic acid under exhaustion and liquid air respectively; D is the coil, G the pin-hole nozzle, and F the valve. By means of this hydrogen jet, liquid air can be quickly transformed into a hard solid. It was shown that

\* 'Proceedings' of the Royal Institution, 1896.

such a jet could be used to cool bodies below the temperature that it is possible to reach by the use of liquid air, but all attempts to collect the liquid hydrogen from the jet in vacuum vessels failed. No other investigator improved on my results,\* or has indeed touched the subject during the last three years. The type of apparatus used in these experiments worked well, so it was resolved to construct a much larger liquid-air plant, and to combine with it circuits and arrangements for the liquefaction of hydrogen. This apparatus took a year to build, and many months have been occupied in the testing and preliminary trials. The many failures and defeats need not be detailed.

On May 10, 1898, starting with hydrogen cooled to  $-205^{\circ}$ , and under a pressure of 180 atmospheres, escaping continuously from the nozzle of a coil of pipe at the rate of about 10 to 15 cubic feet per minute, in a vacuum vessel doubly silvered and of special construction, all surrounded with a space kept below  $-200^{\circ}$ , liquid hydrogen commenced to drop from this vacuum vessel into another doubly isolated by being surrounded with a third vacuum vessel. In about five minutes, 20 cc. of liquid hydrogen were collected, when the hydrogen jet froze up, from the accumulation of air in the pipes frozen out from the impure hydrogen. The yield of liquid was about 1 per cent. of the gas. The hydrogen in the liquid condition is clear and colourless, showing no absorption spectrum, and the meniscus is as well defined as in the case of liquid air. The liquid must have a relatively high refractive index and dispersion, and the density appears at first sight to be in excess of the theoretical density, namely 0.18 to 0.12, which we deduce respectively from the atomic volume of organic compounds, and the limiting density found by Amagat for hydrogen gas under infinite compression. A preliminary attempt, however, to weigh a small glass bulb in the liquid made the density only about 0.08, or half the theoretical. My old experiments on the density of hydrogen in palladium gave a value for the combined element of 0.62. Not having arrangements at hand to determine the boiling point other than a thermo-junction which gave entirely fallacious results, experiments were made to prove the excessively low temperature of the boiling fluid. In the first place if a long piece of glass tubing, sealed at one end and open to the air at the other, is cooled by immersing the closed end in the liquid hydrogen, the tube immediately fills where it is cooled with solid air. A small glass tube filled with liquid oxygen when cooled in liquid hydrogen is transformed into a bluish white solid. This is a proof that the boiling point of hydrogen is much lower than any temperature previously reached by the use of liquid nitrogen evaporating *in vacuo*, seeing oxygen always remains liquid under such conditions. A first trial of putting liquid hydrogen under exhaustion gave no appearance of transition into the solid state. When the vacuum tube containing liquid hydrogen is immersed in liquid air so that the external wall

of the vacuum vessel is maintained at about  $-190^{\circ}$ , the hydrogen is found to evaporate at a rate not far removed from that of liquid air from a similar vacuum vessel under the ordinary conditions of temperature. This leads me to the conclusion that, with proper isolation, it will be possible to manipulate liquid hydrogen as easily as liquid air.

The boiling point of liquid hydrogen at atmospheric pressure in the first instance was determined by a *platinum-resistance thermometer*. This was constructed of pure metal and had a resistance of 5.3 ohms at  $0^{\circ}$  C., which fell to about 0.1 ohm when the thermometer was immersed in liquid hydrogen. The reduction of this resistance to normal air thermometer degrees gave the boiling points  $-238.2^{\circ}$  and  $-238.9^{\circ}$  respectively by two extrapolation methods, and  $-237^{\circ}$  by a Dickson formula.\* The boiling point of the liquid seems therefore to be  $-238^{\circ}$  C. or  $35^{\circ}$  absolute, and is thus about  $5^{\circ}$  higher than that obtained by Olszewski by the adiabatic expansion of the compressed gas, and about  $8^{\circ}$  higher than that deduced by Wroblewski from Van der Waal's equation. From these results it may be inferred that the critical point of hydrogen is about  $50^{\circ}$  absolute, and that the critical pressure will probably not exceed 15 atmospheres.

If we assume the resistance reduced to zero, then the temperature registered by the electric thermometer ought to be  $-244^{\circ}$  C. At the boiling point of hydrogen, registered by the electric-resistance thermometer, if the law correlating resistance and temperature can be pressed to its limits, a lowering of the boiling point of hydrogen by  $5^{\circ}$  or  $6^{\circ}$  C. would therefore produce a condition of affairs in which the platinum would have no resistance, or would become a perfect conductor. Now we have every reason to believe that hydrogen, like other liquids, will boil at a lower temperature the lower the pressure under which it is volatilised. The question arises, how much lowering of the temperature can we practically anticipate? For this purpose we have the *boiling point given by the hydrogen gas thermometer*, and critical data available, from which we can calculate an approximate vapour pressure formula, accepting  $22^{\circ}$  absolute as about the boiling point,  $33^{\circ}$  absolute as the critical temperature, and 15.4 atmospheres as the critical pressure; then, as a first approximation—

$$\log. p = 6.410 - \frac{77.62}{T} \text{ mm.} \quad . \quad . \quad (1)$$

If, instead of using the critical pressure in the calculation, we assume the molecular latent heat of hydrogen to be proportional to the absolute boiling point, then from a comparison with an expression of the same kind, which gives accurate results for oxygen tensions below one atmosphere, we can derive another expression for hydrogen vapour

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\* See Phil. Mag., 45, 525, 1898.



pressures, which ought to be applicable to boiling points under reduced pressure.

The resulting formula is—

$$\log. p = 7.0808 - \frac{88}{t} \text{ mm.} \quad (2)$$

Now formula (1) gives a boiling point of  $14.2^{\circ}$  absolute under a pressure of 25 mm., whereas the second equation (2) gives for the same pressure  $15.4^{\circ}$  absolute. As the absolute boiling point under atmospheric pressure is about  $22^{\circ}$ , both expressions lead to the conclusion that ebullition under 25 mm. pressure ought to reduce the boiling point some  $7^{\circ}$  C. For some time experiments have been in progress with the object of determining the temperature of hydrogen boiling under about 25 mm. pressure, by the use of the platinum thermometer; but the difficulties encountered have been great, and repeated failures very exasperating. The troubles arise from the conduction of heat by the leads; the small latent heat of hydrogen volume for volume as compared with liquid air; the inefficiency of heat isolation; and the strain on the thermometer brought about by solid air freezing on it and distorting the coil of wire. In many experiments, the result has been that all the liquid hydrogen has evaporated before the pressure was reduced to 25 mm., or the thermometer was left imperfectly covered. The apparatus employed will be understood from Fig. 2. The liquid hydrogen collected in the vacuum vessel

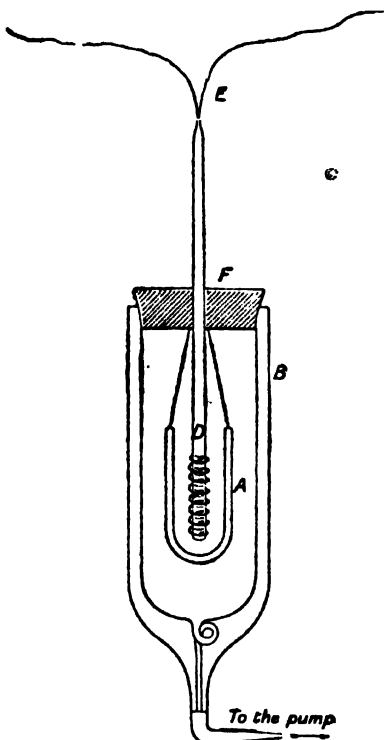


Fig. 2.

A was suspended in a larger vessel of the same kind B, which is so constructed that a spiral tube joins the inner and outer test-tubes of which B is made, thereby making an opening into the interior at C. The resistance thermometer D and leads E pass through a rubber cork F, and the exhaustion takes place through C. In this way the cold

vapours are drawn over the outside of the hydrogen vacuum vessel, and this helps to isolate the liquid from the convective currents of gas. To effect proper isolation, the whole apparatus ought to be immersed in liquid air under exhaustion. Arrangements of this kind add to the complication, so in the first instance the liquid was used as described. The liquid hydrogen evaporated quietly and steadily under a diminished pressure of about 25 mm. Naturally the liquid does not last long, so the resistance has to be taken quickly. Just before the reduction of pressure began, the resistance of the thermometer was 0.181 ohm. This result compares favourably with the former observation on the boiling point, which gave a resistance of 0.129 ohm. On reducing the pressure, the resistance diminished to 0.114 ohm, and kept steady for some time. The lowest reading of resistance was 0.112 ohm. This value corresponds to  $-239.1^{\circ}\text{C.}$ , or only one degree lower on its own scale, than the boiling point at atmospheric pressure, whereas the temperature ought to have been reduced at least  $5^{\circ}$  under the assumed exhaustion according to the gas thermometer scale. The position of the observation on the curve of the relation of temperature and resistance for No. 7 thermometer is shown on the accompanying diagram (Fig. 3). As a matter of fact, however, this platinum thermometer was, when placed in liquid hydrogen, cooled at starting below its own temperature of perfect conductivity, so that no exhaustion was needed to bring it to this point. The question arises then as to what is the explanation of this result? Has the platinum resistance thermometer arrived at a limiting resistance about the boiling point of hydrogen, so that at a lower temperature its changes in resistance become relatively small—the curve having become practically asymptotic to the axis of temperature? That is the most probable supposition, and it further explains the fact that the temperature of boiling hydrogen obtained by the linear extrapolation of the resistance temperature results in values that are not low enough.

As the molecular latent heats of liquids are proportional to their absolute boiling points, the latent heat of liquid hydrogen will be about two-fifths that of liquid oxygen. It will be shown later, however, that we can reach from  $14^{\circ}$  to  $15^{\circ}$  absolute by the evaporation of liquid hydrogen under exhaustion. From analogy, it is probable that the practicable lowering of temperature to be obtained by evaporating liquid hydrogen under pressures of a few mm. cannot amount to more than  $10^{\circ}$  to  $12^{\circ}\text{C.}$ , and it may be said with certainty that, assuming the boiling point  $35^{\circ}$  absolute to be correct, no means are at present known for approaching nearer than  $20^{\circ}$  to  $25^{\circ}$  to the absolute zero of temperature. The true boiling point is in reality about  $-252^{\circ}\text{C.}$ , in terms of the *gas-thermometer scale*, and the latent heat of the liquid is therefore about two-ninths that of an equal volume of oxygen, or one-fourth that of liquid nitrogen. The platinum-resistance thermometer had a zero point of  $-263.2$  platinum degrees, and when immersed in boiling liquid hydrogen, indicated a temperature of  $-256.8^{\circ}$  on the same scale, or  $6.4$  platinum degrees

from the point at which the metal would theoretically become a perfect conductor. The effect of cooling platinum from the boiling point of liquid oxygen to that of liquid hydrogen is to diminish its resistance to one-eleventh.

The difficulties in liquefying hydrogen caused by the presence of air in the gas have been referred to,\* and later experiments had for their object the removal of this fruitful source of trouble. This is by no means an easy task, as quantities amounting to only a fraction of one per cent. accumulate in the solid state, and eventually choke the nozzle of the apparatus, necessitating the abandonment of the opera-

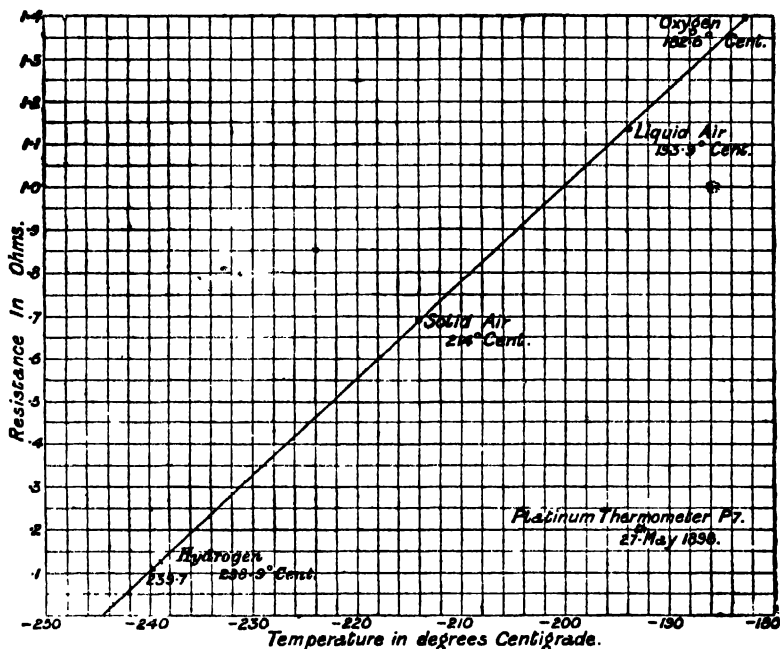


FIG. 3.

tion. Later experiments enabled me to procure a larger supply of liquid hydrogen with which the determination of certain physical constants has been continued. The first observations made with a pure platinum-resistance thermometer had given  $-238^{\circ}$  as the boiling point. A new thermometer, constructed of platinum from a different source, gave practically the same value. As these results might be affected by some constant error, the determination was checked by employing a thermometer constructed from an alloy of rhodium and

platinum, containing 10 per cent. of the former. Alloys had been shown by Professor Fleming and the author to differ from pure metals in showing no sign of becoming perfect conductors at the absolute zero of temperature, and a study of the rhodium-platinum alloy had shown that the change in conductivity produced by cooling from  $0^{\circ}$  to the boiling point of liquid air is regular and may be represented by a straight line. As determined by the rhodium-platinum thermometer, the boiling point of hydrogen was found to be  $-246^{\circ}$  or some  $8^{\circ}$  lower than the platinum thermometer gave. Two ways of explaining the discrepancy between the two values suggested themselves. Pure platinum, although its resistance may be represented by a straight line almost down to the solidifying point of air, shows signs of a departure from regularity at about this point, and the curve may become asymptotic at lower temperatures. On the other hand, the resistance of the rhodium-platinum alloy diminishes less rapidly at these lower temperatures and is much higher than that of pure platinum under similar conditions. It follows that its resistance curve, in all probability, deviates less from a straight line than is the case with platinum. Either cause would explain the differences observed, but the lower boiling point ( $-246^{\circ}$  or  $27^{\circ}$  absolute) seemed to be the more probable as it agreed very fairly with the value for the boiling point calculated by the author from Wroblewski's results. As the use of other pure metals or alloys was not likely to lead to more satisfactory results, the problem had to be attacked in a different way, namely, by means of an "air" thermometer containing hydrogen under diminished pressure.

A first attempt has been made at determining the boiling-point by a constant-volume hydrogen thermometer working under diminished pressure. This thermometer, which gave the boiling point of oxygen as  $90.5^{\circ}$  absolute or  $-182.5^{\circ}$ , gave for hydrogen  $21^{\circ}$  absolute or  $-252^{\circ}$ . The three determinations that have been made are then as follows: (1) pure platinum resistance thermometer,  $35^{\circ}$  absolute; (2) rhodium-platinum resistance thermometer  $27^{\circ}$  absolute; (3) hydrogen thermometer,  $21^{\circ}$  absolute. From this it appears that the boiling point of hydrogen is really lower than was anticipated, and must range between  $20^{\circ}$  and  $22^{\circ}$  absolute. Further experiments will be made with thermometers filled with hydrogen prepared from different sources. A hydrogen thermometer filled with the gas obtained from the evaporation of the liquid hydrogen itself must be employed.

The approximate density of liquid hydrogen at its boiling point was found by measuring the volume of the gas obtained by evaporating 10 cc. of the liquid, and is slightly less than 0.07, or about one-sixth that of liquid marsh-gas, which is the lightest liquid known. It is remarkable that, with so low a density, liquid hydrogen is so easily seen, has so well defined a meniscus, and can be so readily collected and manipulated in vacuum vessels. As hydrogen occluded in palladium has a density of 0.62, it follows that it must

be associated with the metal in some other state than that of liquefaction.

The atomic volume of liquid hydrogen at its boiling point is about 14·3, the atomic volumes of liquid oxygen and nitrogen being 13·7 and 16·6 respectively at their boiling points. The weight of a litre of hydrogen gas at the boiling point of the liquid is about the same as that of air, at the ordinary temperature. The ratio of the density of hydrogen gas at the boiling point to that of the liquid is approximately 1 : 60, as compared with a ratio of 1 : 255 in the case of oxygen under similar conditions.

The specific heat of hydrogen in the gaseous state and in hydrogenised palladium is 3·4, but may very probably be 6·4 in the liquid substance. Such a liquid would be unique in its properties; but as the volume of one gramme of liquid hydrogen is about 14–15 cc., the specific heat per unit volume must be nearly 0·5, which is about that of liquid air. It is highly probable, therefore, that the remarkable properties of liquid hydrogen predicted by theory will prove to be less astonishing when they are compared with those of liquid air, volume for volume, at corresponding temperatures.

With hydrogen as a cooling agent we shall get to from 13° to 15° of the zero of absolute temperature, and its use will open up an entirely new field of scientific inquiry. Even so great a man as James Clerk Maxwell had doubts as to the possibility of ever liquefying hydrogen.\* He says: "Similar phenomena occur in all the liquefiable gases. In other gases we are able to trace the existence of attractive force at ordinary pressures, though the compression has not yet been carried so far as to show any repulsive force. In hydrogen the repulsive force seems to prevail even at ordinary pressures. This gas has never been liquefied, and it is probable that it never will be liquefied, as the attractive force is so weak." In concluding his lectures on the non-metallic elements delivered at the Royal Institution in 1852, and published the following year, Faraday said †: "There is reason to believe we should derive much information as to the intimate nature of these non-metallic elements, if we could succeed in obtaining hydrogen and nitrogen in the liquid and solid form. Many gases have been liquefied: the carbonic acid gas has been solidified, but hydrogen and nitrogen have resisted all our efforts of the kind. Hydrogen in many of its relations acts as though it were a metal: could it be obtained in a liquid or a solid condition, the doubt might be settled. This great problem, however, has yet to be solved, nor should we look with hopelessness on this solution when we reflect with wonder—and as I do almost with fear and trembling—on the powers of investigating the hidden qualities of these elements—of questioning them, making them disclose their secrets and tell their tales—given by the Almighty to man."

\* See Scientific Papers, 2, 412.

† See Faraday's Lectures on the Non-Metallic Elements, pp. 292-3.

Faraday's expressed faith in the potentialities of experimental inquiry in 1852 has been justified forty-six years afterwards by the production of liquid hydrogen in the very laboratory in which all his epoch-making researches were executed. The "doubt" has now been settled; hydrogen does not possess in the liquid state the characteristics of a metal. No one can predict the properties of matter near the zero of temperature. Faraday liquefied chlorine in the year 1823. Sixty years afterwards Wroblewski and Olszewski produced liquid air, and now, after a fifteen years' interval, the last of the old permanent gases, hydrogen, appears as a static liquid. Considering that the step from the liquefaction of air to that of hydrogen is relatively as great in the thermodynamic sense as that from liquid chlorine to liquid air, the fact that the former result has been achieved in one-fourth the time needed to accomplish the latter proves the greatly accelerated pace of scientific progress in our time.

The efficient cultivation of this field of research depends on combination and assistance of an exceptional kind; but in the first instance money must be available, and the members of the Royal Institution deserve my especial gratitude for their handsome donations to the conduct of this research. Unfortunately its prosecution will demand a further large expenditure. It is my duty to acknowledge that at an early stage of the inquiry the Hon. Company of Goldsmiths helped low-temperature investigation by a generous donation to the Research Fund.

During the whole course of the low-temperature work, carried out at the Royal Institution, the invaluable aid of Mr. Robert Lennox has been at my disposal, and it is not too much to say that, but for his engineering skill, manipulative ability and loyal perseverance, the present successful issue might have been indefinitely delayed. My thanks are also due to Mr. J. W. Heath for valuable assistance in the conduct of the experiments.

[J. D.]

Friday, February 10, 1893.

THE HON. SIR JAMES STIRLING, M.A. LL.D., Vice-President,  
in the Chair.

PROFESSOR H. S. HEVE-SHAW, LL.D. M. Inst. C.E.

*The Motion of a Perfect Liquid.*

IF we look across the surface of a river, we cannot fail to observe the difference of the movement at various points. Near one bank the velocity may be much less than near the other, and generally, though not always, it is greater in the middle than near either bank. If we could look beneath the surface and see what was going on there, we should find that the velocity was not so great near the bottom as at the top, and was scarcely the same at any two points of the depth. The more we study the matter, the more complex the motion appears to be; small floating bodies are not only carried down at different speeds and across each other's paths, but are whirled round and round in small whirlpools, sometimes even disappearing for a time beneath the surface. By watching floating bodies we can sometimes realise these complex movements, but they may take place without giving the slightest evidence of their existence.

You are now looking at water flowing through a channel of varying cross section, but there is very little evidence of any disturbance taking place. By admitting colour, although its effect is at once visible on the water, it does not help us much to understand the character of the flow. If, however, fine bubbles of air are admitted, we at once perceive (Fig. 1) the tumultuous conditions under which the water is moving and that there is a strong whirlpool action. This may be intensified by closing in two sides (Fig. 2), so as to imitate the action of a sluice gate, through the narrow opening of which the water has all to pass, the presence of air making the disturbed behaviour of the water very evident.

Now you will readily admit that it is hopeless to begin to study the flow of the water under such conditions, and we naturally ask, are there not cases in which the action is more simple? Such would be the case if the water flowed very slowly in a perfectly smooth and parallel river bed, when the particles would follow one another in lines called "stream-lines," and the flow would be like the march of a disciplined army, instead of like the movement of a disorderly crowd, in which, free fights taking place at various points may be supposed to resemble the local disturbances of whirlpools or vortices.

The model (Fig. 3) represents on a large scale a section of the channel already shown, in which groups of particles of the water are indicated by round balls, lines in the direction of flow of these groups (which for convenience we may call particles) being coloured alternately. When I move these so that the lines are maintained, we imitate "stream-line" motion, and when, at any given point of the pipe, the succeeding particles always move at exactly the same velocity, we have what is understood as "steady motion."

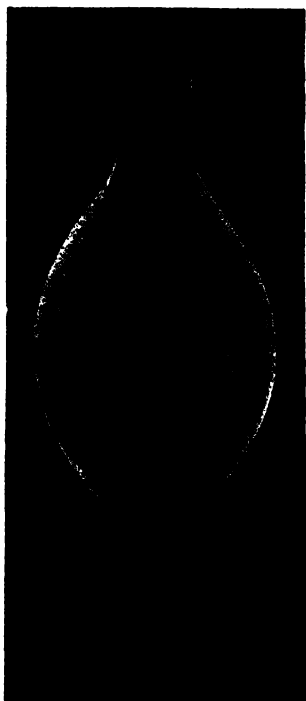


FIG. 1.

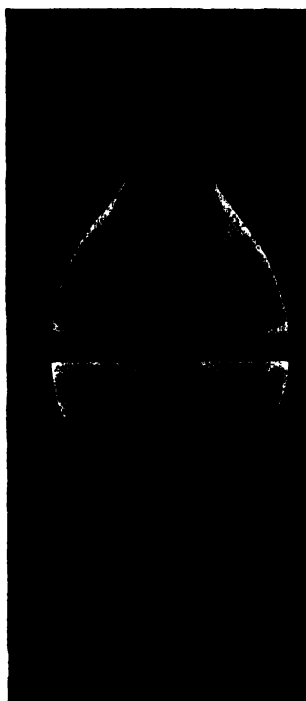


FIG. 2.

As long as all the particles move in the straight portion of the channel, their behaviour is easy enough to understand. But as the channel widens out, it is clear that this model does not give us the proper distribution. In the model, the wider portions are not filled up, as they would be, with the natural fluid; for it must be clearly understood that the stream-lines do not flow on as the balls along these wires, passing through a mass of dead water, but redistribute themselves so that every particle of water takes part in the flow.



Perhaps you may think that if these wires were removed, and the wooden balls allowed to find their own positions, they would group themselves as with an actual liquid. This is not the case; and, for reasons that you will see presently, no model of this kind would give us the real conditions of actual flow. By means of a model, however, we may be able to understand why it is so absolutely essential we should realise the correct nature of the grouping which occurs.

First look at the two diagrams on the wall (Figs. 4 and 5), which you will see represent channels of similar form to the experimental

one. The same number of particles enter and leave in each under apparently the same conditions, so that the idea may naturally arise in your minds, that if the particles ultimately flow with the same speed whatever their grouping in the larger portion of the channel, it cannot much matter in what particular kind of formation they actually pass through that wider portion.

To understand that is really very important. Let us consider a model (Fig. 6) specially made for the purpose. You will see that we have two lines of particles which we may consider stream-lines, those on the left coloured white, and those on the right coloured red. The first and last are now exactly 18 inches apart, there being eighteen balls of 1 inch diameter in the row. If I move the red ones upward, I cause them to enter a wider portion of the channel, where they will have to arrange themselves so as to be three abreast (Fig. 7).

(Fig. 7). It is quite clear to you, that as I do this their speed in the wider portion of the channel is only one-third of that in the narrow portion, as you will see from the relative positions of the marked particles. Now, directly the first particle entered the wider channel, it commenced to move at a reduced speed, with the result that the particles immediately behind it must have run up against it, exactly in the same way that you have often heard the trucks in a goods train run in succession upon the ones in front, when the speed of the engine is reduced; and you will doubtless have noticed that it was not necessary for the engine actually to stop in order that this might take place. Moreover, the force of the impact depended largely upon the suddenness with which the

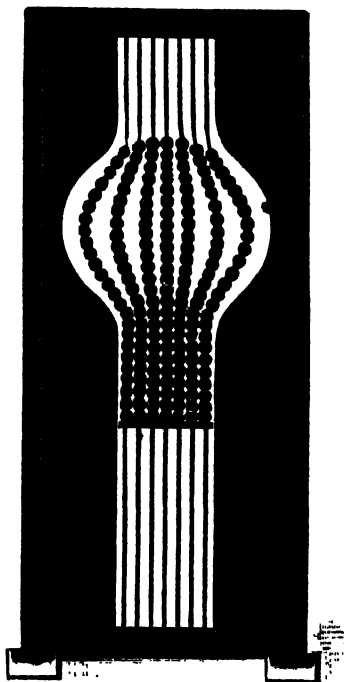


FIG. 3.

speed of those in front was reduced. Applying this illustration to the model, you will see that the impact of these particles in the wider portion would necessarily involve a greater pressure in that part. Turning next to the white balls, I imitate, by means of the left-hand portion, the flow which will occur in a channel six times as large as the original one, and you now see (Fig. 7) that as the particles have placed themselves six abreast, and the first and last row are 3 inches apart instead of 18 inches, the speed in the wider portion of the channel must have been one-sixth of that in the narrow portion. Evidently, therefore, the velocity of the particles has been reduced more rapidly than in the previous case, and the pressure must consequently be correspondingly greater.

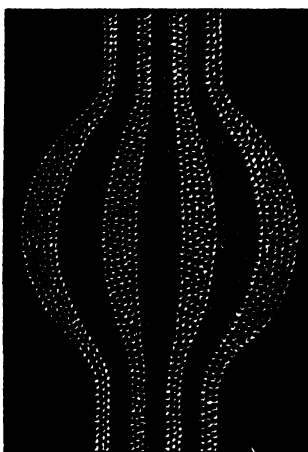


FIG. 4.

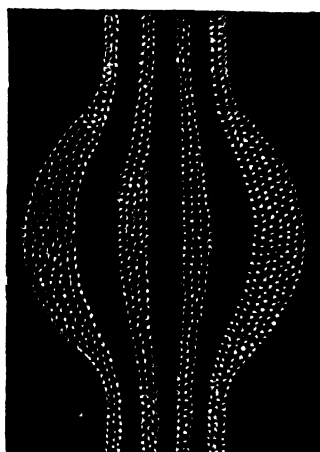


FIG. 5.

We may now take it as perfectly clear and evident, that the pressure is greater in the wider portion and less in the narrower portion of the channel. Turning now to the two diagrams, we see that the pressure is in each case greater in every row of particles as in the wider portions of the channel, but that instead of being suddenly increased, as in the model, it is gradually increased. The width of the coloured bands, that is, rows of particles, or width apart of stream-lines, is a measure of the increased pressure. Thus you will now regard the width of the bands, or what is the same thing, the distance apart of the stream-lines, as a direct indication of pressure, and the narrowness or closeness of the stream-lines as a direct indication of velocity.

Next notice the great difference between the two diagrams. In one diagram (Fig. 4), the change of width is uniform across the entire

section. In diagram (Fig. 5), however, this is not the case. In the narrowest portion of the channel in each diagram, there are seven colour bands of little balls each containing three abreast, but we find that in one diagram (Fig. 4) they are equally spaced in the wider part six abreast throughout. In the other diagram (Fig. 5), the outer row is spaced eight abreast, the second row rather more than six, and the inner rows rather more than four abreast, and the middle row less than four abreast, making in all forty-two in a row, as in the previous case. One diagram (Fig. 6), therefore, will represent an entirely different condition to the state represented by the other diagram (Fig. 4), the pressure in the wide part of the latter varying from a maximum at the outside to a minimum in the middle, while the corresponding velocity is greatest in the middle and least at the outside or borders.

Now, when we know the pressure at every point of a liquid, and

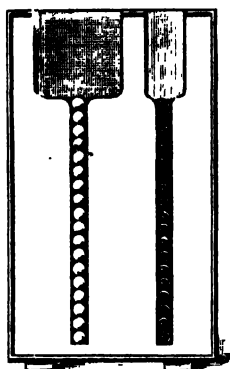


FIG. 6.

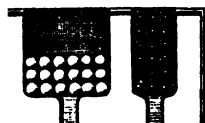


FIG. 7.

also the direction in which the particles are moving, together with their velocity at every point, we really know all about its motion, and you will see how important the question of grouping is, and that, in fact, it really constitutes the whole point of my lecture to-night. How then shall we ascertain which of the two groupings (Fig. 4 or 5) is correct, or whether possibly some grouping totally different from either does not represent the real conditions of flow?

Now, the model does not help us very far, because there seems to be no means of making the grouping follow any regular law which might agree with fluid motion. In whatever way we improve such a model, we can scarcely hope to imitate by merely mechanical means the motion of an actual liquid, for reasons which I will now try to explain.

In the first place, apart from the particles having no distinguishing characteristics, either when the liquid is opaque or transparent, they are so small and their number is so great as to be almost beyond our

powers of comprehension. Let me try, by means of a simple illustration, to give some idea of their number, as arrived at by perfectly well recognised methods of physical computation. Lord Kelvin has used the illustration that, supposing a drop of water were magnified to the size of the earth, the ultimate particles would appear to us between the size of cricket balls and footballs. I venture to put the same fact, in another way, that may perhaps strike you more forcibly. This tumbler contains half a pint of water. I now close the top. Suppose that, by means of a fine hole, I allow one and a half billion particles to flow out per second—that is to say, an exodus equal to about one thousand times the population of the world in each second,—the time required to empty the glass would be *between* (for of course we can only give certain limits) seven million and forty-seven million years.

In the next place, we have the particles interfering with each other's movements by what we call "viscosity."

Of course, the general idea of what is meant by a "viscous" fluid is familiar to everybody, as that quality which treacle and tar possess in a marked degree, glycerine to a less extent, water to a less extent than glycerine, and alcohol and spirits least of all. In liquids, the property of viscosity resembles a certain positive "stickiness" of the particles to themselves and to other bodies; and would be well represented in our model by coating over the various balls with some viscous material, or by the clinging together, which might take place by the individuals of a crowd, as contrasted with the absence of this in the case of no viscosity as represented by the evolutions of a body of soldiers. It may be accounted for, to a certain extent, by supposing the particles to possess an irregular shape, or to constantly move across each other's paths, causing groups of particles to be whirled round together.

Whatever the real nature of viscosity is, it results in producing in water the eddying motion which would be perfectly impossible if viscosity were absent, and which makes the problem of the motion of an imperfect liquid so difficult and perplexing.

Now, all scientific advance in discovering the laws of nature has been made by first simplifying the problem and reducing it to certain ideal conditions, and this is what mathematicians have done in studying the motion of a liquid.

We have already seen what almost countless millions of particles must exist in a very small space, and it does require a much greater stretch of the imagination to consider their number altogether without limit. If we then assume that a liquid has no viscosity, and that it is incompressible, and that the number of particles is infinite, we arrive at a state of things which would be represented in the case of the model or the diagram on the wall, when the little globes were perfectly smooth, perfectly round and perfectly hard, all of them in contact with each other, and with an unlimited number occupying the smallest part of one of the coloured or clear bands. This agrees with

the mathematical conception of a perfect liquid, although the mathematician has in his mind the idea of something of the nature of a jelly consisting of such small particles, rather than of the separate particles themselves. The solution of the problem of the grouping of the little particles, upon which so much depends, and which may have at first seemed so simple a matter, really represents, though as yet applied to only a few simple cases, one of the most remarkable instances of the power of higher mathematics, and one of the greatest achievements of mathematical genius.

You will be as glad as I am that it is not my business to-night to explain the mathematical processes by which the behaviour of a perfect liquid has been to a certain extent investigated. You will also understand why such models as we could actually make, or any analogy with the things with which we are familiar, would not help us very much in obtaining a mental picture of the behaviour of a perfect liquid. If, for instance, we try to make use of the idea of drilled soldiers, and move the lines with that object in view, we see that instead of the ordinary methods of drill, the middle rank soon gains on the others, and enters again the parallel portion of the channel in a very different relative position to the opposite lines, although the stream-lines would all have the same actual velocity when once again in the parallel portion. Since, then, we cannot use models or any simple analogy with familiar things, or follow—at any rate this evening—the mathematical methods of dealing with the problem, what way of understanding the subject is left to us?

If we take two sheets of glass, and bring them nearly close together, leaving only a space the thickness of a thin card or piece of paper, and then by suitable means cause liquid to flow under pressure between them, the very property of viscosity, which as before noted, is the cause of the eddying motion in large bodies of water, in the present case greatly limits the freedom of motion of the fluid between the two sheets of glass, and thus prevents not only eddying or whirling motion, but also counteracts the effect of inertia. Every particle is then compelled by the pressure behind and around it to move onwards without whirling motion, following the path which corresponds exactly with the stream-lines in a perfect liquid.

If we now, by a suitable means, allow distinguishing bands of coloured liquid to take part in the general flow, we are able to imitate exactly the conditions represented in the diagrams (Figs. 4 and 5). You are now looking at a projection on the screen (Fig. 8, Plate I.) of liquid, which, in flowing through the gradually enlarging and contracting channel, is obeying the conditions I have described. Such is the steadiness of its motion, that it is scarcely possible to believe at first that the figure does not consist of fixed bands of colour painted in perfectly smooth curves. By varying the flow of the coloured liquid however, you will realise at once that the painting is done by nature and not by the hand of a human artist.

Now you will notice that the bands widen out as they approach the

wider portion of the channel, afterwards contracting to their original width; but I have already prepared you for the fact that they do not do this uniformly, and, in spite of the fact that they were all equally spaced in the narrower portion of the pipe, they are very unequally spaced in the wider portion—in this you will see the resemblance to the model, Fig. 3, and the case given in Fig. 5.

You will not, I trust, now fall into the very natural mistake of thinking that the nature of the substance is more attenuated because the band has become wider, but will realise that the particles are in the wider portion just as close together as in the narrower. I have already explained that as more particles are required to fill the greater width, and can only be supplied from the same band behind, the band at that part cannot possibly be moving as fast as the narrow bands at the same cross-section, that is, on the line drawn across at right angles to the central line of the stream.

This I will now prove to you by a very simple but conclusive experiment, for by opening and closing the tap regulating the colour bands, we can start a fresh supply exactly at the same instant in each of the bands—in the same way as the starter attempts, though usually not with the same success, to carry out his duties on the racecourse. (Fig. 9, Plate I.) shows the different position of various colour band fronts which were all started in line, and gives a good idea of the relative changes of velocity. You will see that the straight formation of the row is not maintained, even in the parallel portion of the channel, the middle row gaining on the sides, which is not because of any resistance on the sides, but because the influence of the enlargement is felt before that is actually reached. Then, you see, the middle portion slows down considerably, and, for an instant, of course, the portions which lag behind on the sides appear to be overtaking it; they in turn, however, have to occupy so much more space on the sides, that they fall rapidly behind and the once straight row of particles becomes, in leaving, more and more curved. This curve is so drawn out as to leave no doubt in your minds as to which band of particles wins the race; and, although ultimately these particles are again flowing along the narrow channel at the same velocity, whether in the middle or at the sides, the particles which started at the middle, at the same time as the particles at the sides, have obtained the lead in finally entering the channel again. This lead they will continue to maintain, unless they should encounter an obstacle in the middle of the channel, when, as I shall be able to show you in a subsequent experiment, their positions may possibly be reversed.

By now gradually closing in the slides, so as to reproduce conditions of a narrow diaphragm or channel with ordinary flow, instead of the turbulent or whirlpool motion which then resulted, the colour bands at once respond to the altered conditions (Fig. 10), and, like a perfectly drilled body of troops, perform the required evolutions immediately, even though the defile through which they are compelled to pass involves almost incredibly rapid change of speed. So great, indeed, is

the confidence which we may place upon their behaviour, that the enlargement from the original channel, Figs. 1 and 2, as you see, has been much exaggerated in order to make the conditions as severe as possible, and intensify the effect. The greater pressure in the wider portion may be illustrated by the fact, that while the plugs remain at rest in the middle, where the narrow bands are, they are forced out, when removed to the sides, by the greater pressure, which there acts on the ends. This is where the bands were widest and the velocity slowest. This is quite contrary to what might have been expected, seeing that the liquid was forced so rapidly through the narrower channel, but it needs many illustrations to bring home to us this apparent contradiction of our ordinary experience. Fig. 11 shows the liquid now flowing out through the new channel thus made, as well as through the original place of exit.

But at this stage you may reasonably enquire how it is that we are able to state, with so much certainty, that the artificial conditions of flow with a viscous liquid are really giving us the stream-line motion of a perfect one; and this brings me to the results which mathematicians have obtained.

The view now shown represents a body of circular cross-section, past which a fluid of infinite extent is moving, and the lines are plotted from mathematical investigation and represent the flow of particles. This particular case gives us the means of most elaborate comparison; although we cannot employ a fluid of infinite extent, we can prepare the border of the channel to correspond with any one of the particular stream-lines, and measure the exact positions of the lines inside.

By means of a second lantern, the real flow of a viscous liquid for this case is shown upon the second screen, and you will see that it agrees with the calculated flow round a similar obstacle of a perfect liquid. The diagram shown on the wall is the actual figure employed for comparison and upon which the experimental case was projected. By this means, it was proved that the two were in absolute agreement. If we start the impulses, as before, in a row, we at once see how the middle particles lag behind the outer ones, as indicated by the width of the bands, showing that it is not necessarily the side stream-lines that move more slowly. It may be more interesting to you to see, in addition to the foregoing case—in which for convenience, and as quite sufficient for measurement only, a semi-cylinder was employed—the case of a complete cylinder, and this is now shown (Fig. 12, Plate I.). In this case two different colours are used in alternate bands, and these bands are sent in, not steadily but impulsively, in order to illustrate what I have just pointed out. You will see how the greater width of the colour bands before and behind the cylinder indicates an increase of pressure in those regions. This in a ship-shape form accounts for the standing bow and stern waves, whereas the narrowing of the bands at the sides indicates an increase of velocity and reduction of pressure, and accounts for the depression of water level, with which you are doubtless familiar at the corresponding part of a ship.

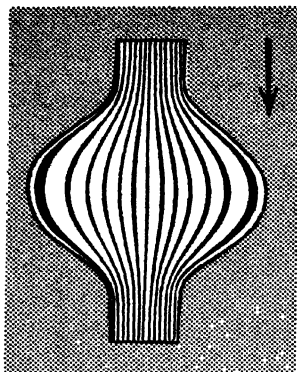


FIG. 8.

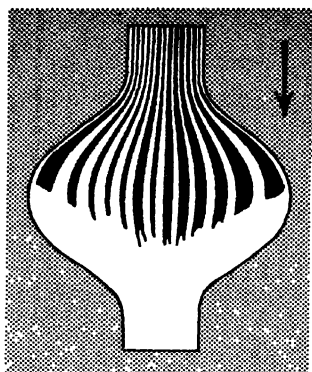


FIG. 9.

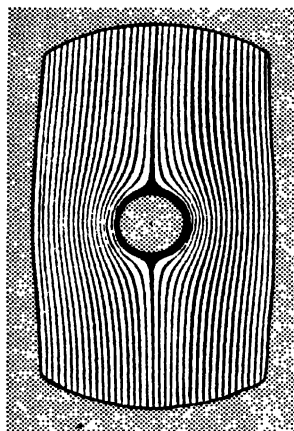


FIG. 12.

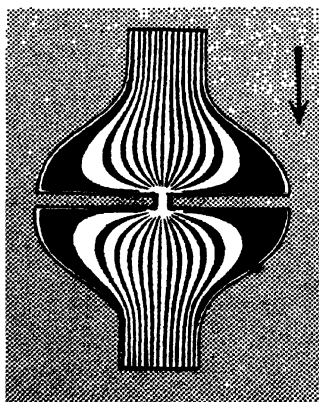


FIG. 10.

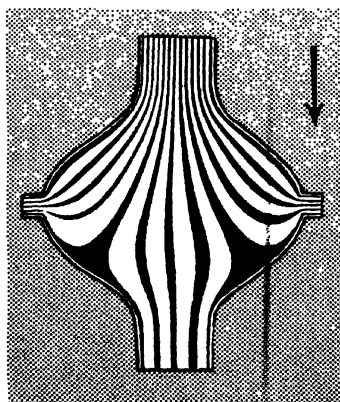


FIG. 11.



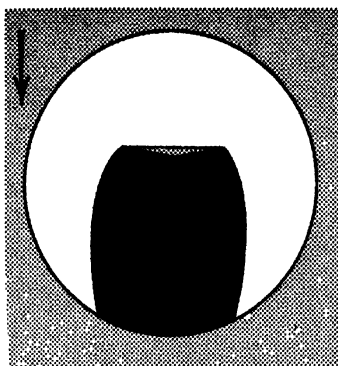


FIG. 14.



FIG. 15.

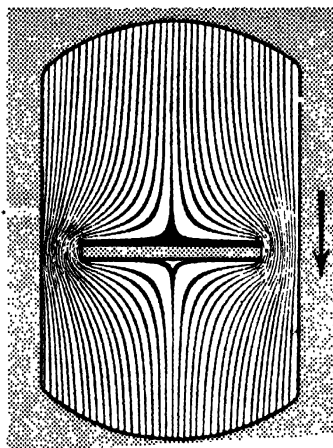


FIG. 16.

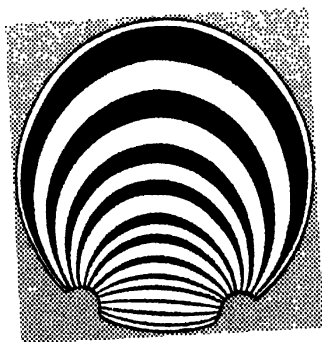


FIG. 17.

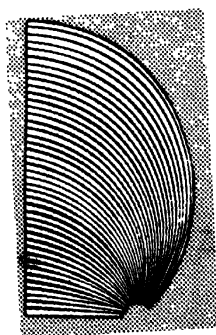


FIG. 18.

I will now take a more striking case. If, instead of a circular body, we had a flat plate, the turbulent nature of the flow is evidently very great, as you will see from the view (Fig. 13), which is a photograph of the actual flow under these conditions, made visible by very

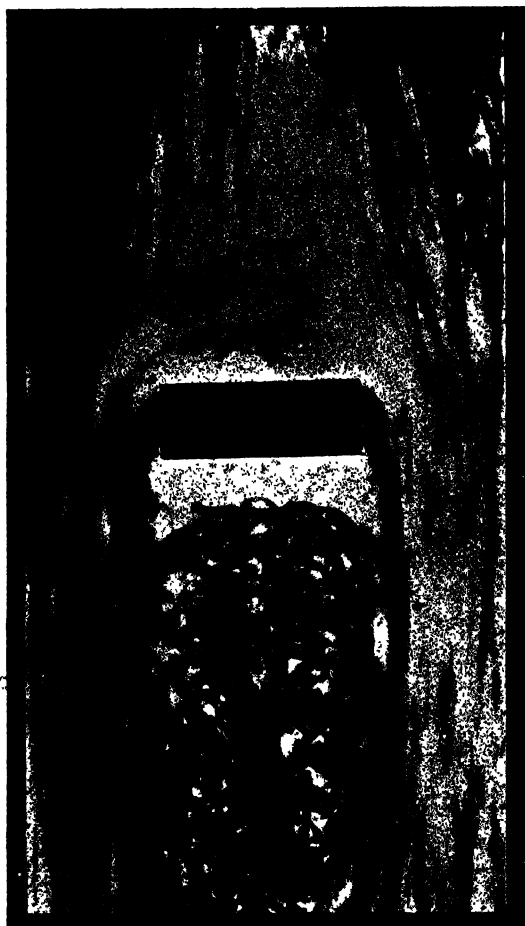


FIG. 13.

fine air bubbles, and showing water at rest in the clear space behind the obstacle.

We can, however, take steps to reduce this turbulence, and you now see on the second screen the flow by means of apparatus which time

does not permit me to describe, but which gives a slow and steady motion that it would be impossible to improve upon in actual conditions of practice, or even, I am inclined to think, by any experimental method. Instead of using air to make this flow clear, we now allow colour to stream behind the plate, and you will see (Fig 14, Plate II.) that the water still refuses to flow round to the back, and spreads on either side. We have so slow a velocity as not to induce vortex motion, but the inertia of the particles which strike the flat plate causes them to be deflected to either side, exactly as tennis balls in striking against a wall obliquely. The sheet of water is so thick, that is to say, the parallel glass plates are so far apart, that they do not enable the viscosity of the water to act as a sufficient drag to prevent this taking place.

To make the action of the water in front of the plate more visible, a different coloured liquid is allowed to enter from orifices in a small pipe placed across the slide in the thick sheet. You will now see that the general motion is steady enough to give a very clear idea of the deflecting action of the plate, and streaks of colour set themselves in such a way as to indicate the behaviour of the individual particles. This effect is practically what is called "discontinuity," for, although perfectly discontinuous motion can only take place when there is no viscosity, the effect of the general flow upon the nearly quiescent mass behind the plate is very slight.

If we send the flow in impulses, we produce vortex motion at the edge, due to viscosity, as shown in Fig. 15. This takes place in the thick sheet directly the velocity is sufficiently increased, though only at the edges of the plate, the motion being otherwise the same.

Mathematicians, however, predicted with absolute certainty, that with stream-line motion the water should flow round and meet at the back, a state of things that, however slow we make the motion in the present case, does not occur owing to the effect of inertia. They have drawn with equal confidence the lines along which this should take place. We could either effect this result with the experiment you have just seen, by using a much more viscous liquid, such as treacle, or, what comes to the same thing, bringing the two sheets of glass nearly close together; and the flow which you are now witnessing (Fig. 16, Plate II.) shows the result of doing this. The colour bands in front of the plate no longer mix at all with the general body of flow, or are unsteady, as was the case in the last experiment, but flow round the plate and flow so steadily, that, unless we jerk the flow of the colour bands, it is impossible to tell in which direction they are actually moving.

A still more extraordinary case is that of a plate at an angle of 45 degrees, the central line no longer striking the plate at the centre, but at a certain point when, together with the actual curves of flow, has been calculated and plotted by Professor Lamb. The calculations being made for an infinite fluid, we require the artificial border to be prepared, corresponding to the different stream-lines, and when

that is done, we find that the flow absolutely agrees with that predicted by Professor Lamb, the central line which meets the plate, leaving it exactly with the same form at a corresponding point on the back, the curves of each being hyperbolas. This effect is, of course, produced by the central line dividing on the plate, a portion flowing upwards and a portion downwards, reuniting at a corresponding point behind, from whence it flows away.

Such a state of things would be absolutely impossible to conceive by most of us, but by turning the plate at an angle in the lantern, we are able to approximately represent, even without artificial border lines, this condition of flow. You are thus able to see a striking example of the absolute accuracy of mathematical prediction, and to feel every confidence, that the original experiment in the channel, or indeed any others with thin viscous films, should give us indeed a correct picture of what we can never hope to see, viz. the motion of a perfect liquid.

It is satisfactory to know that the principle of the thin films has been examined by probably the greatest authority on the subject, and as a result, Professor Sir G. Gabriel Stokes states, that "they afford a complete graphical solution, experimentally obtained, of a problem which, from its complexity, baffles the mathematician except in a few simple cases."

Whilst I have been dealing with the stream-lines of a perfect liquid, your minds will doubtless have turned to the lines along which magnetic and electrical forces appear to act. We are possibly further from realising the actual nature of these forces, than from a correct conception of the real nature of a liquid. We have long agreed to abandon the old ideas of the electrical and magnetic fluids flowing along these lines, and to substitute instead the idea, that these lines represent merely the directions in which the forces act. Now we can easily see that this conception is quite a reasonable one, for in the case of the model it is not necessary to have the row of balls actually moving, in order that the effect may be transmitted along the different lines they occupy. If I attempt to raise the plate upon which they rest, the pressure is instantly transmitted through the whole row to the top ball along each line, whatever curve the line may take. In the same way, you will remember that it was not necessary to have the colour bands actually in motion, for, though apparently free to move in any direction, they retain their form for a considerable time, and the path along which they would influence each other as soon as the tap is opened, would be along those lines in which the liquid was flowing before it was brought to rest. Hence it is possible, with some suitable means, to cause a viscous liquid to reproduce exactly the lines of magnetic and electrical induction. In the case of magnetism and electricity, it is of course possible, by means of a small magnetic needle or a galvanometer, by exploring the whole surface through which magnetic induction or electrical flow is acting, to plot the lines of force for innumerable cases, where we can work in air or on the surface of the solid conductor.

But in this building it seems natural to take as an example the case first used by the great man to whom the conception of lines of magnetic force is due, for the first reference I have been able to find to such lines is in one of Faraday's earliest papers on the induction of electric currents,\* in which he says, "By magnetic curves I mean the lines of magnetic forces, however modified by the juxtaposition of poles, which would be depicted by iron filings, or those to which a very small magnetic needle would form a tangent."

You are all familiar with the way in which iron filings set themselves, when shaken over the North and South poles of a magnet. The magnetic lines are then nearly, but not quite, circular curves between the two poles. Now, the mathematics of the subject tells us that if the poles could be regarded as points, the lines of force between them would be perfect circles.

You are now looking (Fig. 17, Plate II.), at the colour bands, the edges—or indeed any portion—of which represent lines obtained by admitting coloured liquid from a series of small holes round a central small orifice, which admits clear liquid, and allows them to escape through another small orifice (called respectively in hydromechanics a *source* and *sink*), and I leave it to you to judge how far these curves deviate from the ideal form.

My assistant is now allowing the colour to flow, first steadily and then in a series of impulses, and the latter gives us the conception of waves or impulses of magnetic force, though of course the magnetic transmission force would be instantaneous. Regarded as a liquid, it is here again clear how absolutely the truth of our views concerning the slower movement in the wider portion is verified by this experiment.

A last experiment (Fig. 18) shows the streams admitted, not from a source but from a row of orifices in what corresponds to the slowest moving portion of the flow. The result is, that the colour bands are much narrower, and although the circular forms of the curves are, as in the previous experiment, preserved, the lines are so fine at the point of exit, which, as before, corresponds to the South Pole, as to really approximate to ideal stream-lines.

The same method enables us to trace the lines of force through solid conductors, for, as long as we confine ourselves to two dimensions of space, we may have *flat* conductors of any shape whatever. But it does something more, for by making the film rather deeper in some places than others, more particles arrange themselves there, and the lines of flow will naturally tend in the direction of the deeper portion. This will give the stream lines identically the same shape as the magnetic or electrical curves which encounter in their paths a body of less resistance, for instance, a para-magnetic body.

If, on the other hand, at these points the film is made rather

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\* 'Experimental Researches in Electricity,' vol. i. p. 32

thinner, less particles will be able to dispose of themselves in the shallow portion of the film, and hence the lines of flow will be pushed away from this portion, giving us exactly the same forms as magnetic lines of force in a magnetic field in proximity to a diamagnetic body.

Here, again, mathematical methods have enabled lines of actual flow to be predicted, and you may compare the actual flow for the case of a cylindrical para-magnetic body, which was worked out some years ago.

You will doubtless not be inclined to question the practical value of stream-lines in the subject which we have just been considering, because, unlike the flow of an actual liquid, magnetic lines of force can never be themselves seen, and because there is no doubt as to the correspondence of the directions to the lines of a perfect liquid. It was the conception of these lines in the mind of Faraday, and more particularly their being cut by a moving wire, that enabled him to realise the nature of the subject more clearly than any other man at the time, and to do so much towards the rapid development of electrical science and its practical applications.

When we come to consider the relation of the study of the motion of a perfect liquid with hydromechanics and naval architecture, it must be admitted that the matter is a difficult one. Probably one of the most perplexing things in engineering science is the absence of all apparent connection between higher treatises on hydrodynamics and the vast array of works on practical hydraulics. The natural connection between the treatises of mathematicians and experimental researches of engineers would appear to be obvious, but very little, if any such connection exists in reality, and while at every step electrical applications owe much to the theories which are common to electricity and hydromechanics, we look in vain for such applications in connection with the actual flow of water.

Now the reason for this appears to be the immense difference between the flow of an actual liquid and that of a perfect one owing to the property of viscosity. A comparison of the various experiments which you have seen to some extent indicates this.

In the first place let us consider for a moment some of the things which would happen if water were a perfect liquid. In such a case, a ship would experience a very different amount of resistance, because, although waves would be raised, owing to the reasons which we have already seen, the chief causes of resistance, viz. skin friction and eddying motion, would be entirely absent, and of course a submarine boat at a certain depth would experience no resistance at all, since the pressures fore and aft would be equal. On the other hand, there would be no waves raised by the action of the wind, and there would be no tidal flow, but to make up for this rivers would flow with incredible velocity, since there would be no retarding forces owing to the friction of the banks. But the rivers themselves would soon cease to flow because there would be no rainfall such as exists at

present, since it is due to viscosity that the rain is distributed, instead of falling upon the earth in a solid mass when condensed. In a word, it may be said that the absence of viscosity in water would result in changes which it is impossible to realise.

We may now briefly try to consider the difference between practical hydraulics and the mathematical treatment of a perfect liquid. The earliest attempts to investigate in a scientific way the flow of water appears to have been made by a Roman engineer about 1800 years ago, an effort being made to find the law for the flow of water from an orifice. For more than 1500 years, however, even the simple principle of flow according to which the velocity of efflux varies as the square of the head, or what is the same thing, the height of surface above the orifice varies as the square of the velocity, remained unknown. Torricelli, who discovered this, did so as the result of observing that a jet of water rose nearly to the height of the surface of the body of water from which it issued, and concluded therefore that it obeyed the then recently discovered law of all falling bodies.

Though it was obvious that this law did not exactly hold, it was a long time before it was realised that it was the friction or viscosity of liquids that caused so marked a deviation from the simple theory. Since then problems in practical hydraulics, whether in connection with the flow in rivers or pipes, or the resistance of ships, have largely consisted in the determination of the amount of deviation from the foregoing simple law.

About 100 years ago it was discovered that the resistance of friction varies nearly in accordance with the simple law of Torricelli and also—although for a totally different reason—the resistances due to a sudden contraction or enlargement of cross section of channel or to any sudden obstructions appear to follow nearly the same law. Now it is extremely convenient for reasons which will be understood by students of hydraulics, to treat all kinds of resistance as following the same law, viz. square of velocity which the variation of head or height of surface has shown to do. But this is far from being exact, and an enormous amount of labour has consequently been expended in finding for all conceivable conditions in actual work tables of co-efficients or empirical expressions which are required for calculations of various practical questions. Such data are continually being accumulated in connection with the flow of water in rivers and pipes, for hydraulic motors and naval architecture. This is the practical side of the question.

On the other hand, eminent mathematicians since the days of Newton and the discovery of the method of the calculus, have been pursuing the investigation of the behaviour of a perfect liquid. The mathematical methods which I have already alluded to as being so wonderful, have however scarcely been brought to bear with any apparent result upon the behaviour of a viscous fluid. Indeed, the mathematician has not been really able to adopt the method of the practical investigator, and deal with useful forms of bodies such as

those of actual ships, or of liquid moving through ordinary channels of varying section, even for the case of a perfect liquid, but he has had to take those cases, and they are very few indeed, that he has been able to discover which fit in with his mathematical powers of treatment.

This brief summary may possibly serve to indicate the nature of the difficulties which I have pointed out, and will show you the vast field there yet lies open for research in connection with the subject of hydromechanics, and the great reception which awaits the discovery of a theoretical method of completely dealing with viscous liquids, instead of having recourse as at present principally to empirical formula based on the simple law already alluded to.

We may, however, console ourselves with the thought, that in the application of the laws of motion themselves to *any* terrestrial matters, the friction of bodies must always be taken into account, and renders it necessary, that we should commence by studying the ideal conditions. In this as in other matters the naval architect and engineer must always endeavour as far as possible to base their considerations and work upon the secure foundation of scientific knowledge, making allowances for disturbing causes, which then cease to be the source of perplexity and confusion. From this point of view, the study of the behaviour of a perfect liquid, even when no such form of matter appears to exist, has an interest for the practical man in spite of the deviation of actual liquids from such ideal conditions. If the truth must be told, it is such a deviation from the simple and ideal conditions that really constitute the work of a professional man, and it is only practical experience which, based upon sound technical knowledge, enables 50,000 tons of steel to be made to span the Firth of Forth, Niagara to be harnessed to do the work of 100,000 horses, or an 'Oceanic' to be slid into the sea with as little misgiving as the launch of a fishing boat.

I have, I am afraid, brought you only to the threshold of a vast subject, and in doing so, have possibly employed reasoning of too elementary a kind. After all, I may plead that I have followed the dictum of Faraday, who said, "If assumptions must be made, it is better to assume as little as possible." If I have assumed too little knowledge on your part, it is because of the difficulties I have found in the subject myself. If I have left more obscure than I have been able to make clear, it is consoling to think how many centuries were required to discover even what is known at the present time, and we may well be forgiven if we cannot grasp at once results which represent the life-work of some of the greatest men.



Friday, February 24, 1899.

SIR WILLIAM CROOKES, F.R.S., Vice-President, in the Chair.

PROFESSOR OLIVER LODGE, D.Sc. LL.D. F.R.S.

*Coharers.*

A COHERER is an instrument which responds to electric waves somewhat in the same manner as a microphone responds to sound waves.

A coherer is a light metallic contact or series of contacts introduced into an electric circuit of low voltage containing also a galvanometer or other signalling instrument. A steady current is normally unable to pass, or only very feebly, by reason of the high resistance of the bad joint, but under the influence of a sudden change of potential, or an electric jerk, the resistance of the joint suddenly diminishes, transmitting a considerable current, and signalling the arrival of the electric wave which may have caused the jerk. A slight shake or tap is sufficient to reduce the coherer to its former high resistance.

All metals do not behave in the same way, but the majority thus show an increase of coherence under electric influence, and a sudden decrease under mechanical influence. A few metals (e.g. silver) appear to behave in an opposite direction.

The earliest instances of electrical cohesion exhibited by the lecturer was the small vertical fountain issuing from a smooth orifice, which was found by Lord Rayleigh to scatter its drops by mutual collision except when they were under the influence of an electric field such as that due to a piece of sealing-wax held within a yard or two of the place where the jet breaks into drops. Another variety was the pair of horizontal jets, which, when they impinge, unite or rebound according as there is or is not a difference of potential between them of one or two volts. A pair of soap bubbles in contact were also shown by Mr. Boys to cohere and become one directly a stick of sealing-wax was produced in their neighbourhood.

The two halves of a mercury globule on a flat surface, cut into two with a greasy knife, and the parts connected to the poles of a battery, were found by Lord Rayleigh and by Mr. Appleyard to re-unite directly they were connected to the terminals of one or two Grove cells; a slight delay in the union suggesting that a film of foreign matter was being squeezed out from between the globules under the force of electrostatic attraction.

The electrified dust and smoke experiment, whereby a thick fog in a chamber can be cleared by the discharge from a point, as observed by Lodge and Clark in 1883, was also shown; and the lightning guard experiment with a couple of Leyden jars and a galvanometer and two surfaces in light contact, by which the lecturer observed electrical cohesion of metals in 1888, was exhibited, together with a couple of resonant Leyden jars, one of them charged and sparking, the other responding by closing the circuit of a local battery and ringing a bell; which bell, by its vibration, could effect the tapping back.

The discovery that this property of metals served as the best detector for Hertz waves was made by Monsieur Edouard Branly, Professor of Physics in the Catholic Institute of Paris; and some of Monsieur Branly's original apparatus was exhibited, especially a piece of ebonite smeared over with porphyrised copper so as to form a high resistance, which fluctuated in value between certain limits under the influence of alternate electric sparks and tapping. A Branly filings-tube connected to a speaking galvanometer was shown receiving signals from a Hertz emitter at a distance, the coherer being tapped back automatically in one of many alternative ways. A recent experiment of Signor Tomasina, displaying the effect of electric cohesion was projected on the screen:—A vertical wire about nine inches long had its end immersed in filings and was slowly raised. If a sphere of suitable size were sparking in the neighbourhood, between polished knobs, the electric jerks collected by the vertical wire would give, as Hertz showed, minute perhaps ultra-microscopic sparks to anything brought close to its end. The filings subjected to this action are found to cohere, and can be pulled up in a narrow string, of length depending on the steadiness of the movement.

(M. Tomasina has recently repeated this experiment under liquid, and obtained chains of filings several inches long.)

Another variety of the cohesion experiment under electrical influence, was shown by the lecturer in a form which suggested that electrostatic attraction played a considerable part. A very fine platinum wire was suspended in a glass box, with its lower end close to a flat and highly polished facet of a brass knob. On looking at this wire under a microscope, it and its image in the polished face could both be seen, a slight distance apart; or they could be projected with a strong lens upon a screen. Under the action of electric waves, the gap between the wire and its image sharply disappeared, and the wire was seen clinging to the knob until tapped back. A wire of this kind constitutes an extremely sensitive electroscope, but for this purpose the coherence which sets in (unless silver or some such non-cohering metal is employed) is inconvenient.

Finally a layer of filings on a horizontal glass surface, with tin foil electrodes, was projected on the screen, and subjected to strong electric influence, under which they were seen to move so as to close

up gaps, and were then found to have cohered; for if the superfluous filings were then gently removed, a continuous chain of irregular shape remained reaching from one terminal to the other. By suitably choosing the filings their motion when subjected to very slight electric sparks can readily thus be seen, and if subsequently a point be used to sweep them sideways, they are found to be quite in a different condition to ordinary unelectrified filings, for they are matted together into a sort of coherent mass just like the dust particles in a bell-jar under the influence of an electrified point, or somewhat like iron filings in a magnetic field. A stronger spark often destroys this cohesion, scattering the particles asunder, and producing somewhat the same effect as a mechanical tap, though for a different reason. Filings thus electrically disorganised are not usually in a sensitive condition. A set of large brass shavings on a flat surface, with sparks sent through them, at first show lines of spark in all directions, but gradually under the cohering influence are able to close up and presently conduct the discharge without visible manifestation.

Thus the process going on more or less in coherers, either the single-point or the multiple point kind, can be made to some extent apparent to the eye.

Some of the old apparatus used by the lecturer to send signals by Hertz waves and coherers over small distances (the now so-called wireless telegraphy) which had been exhibited to the Institution on Friday evening, June 1st, 1894, were once more exhibited, the receiver being carried about into different parts of the room: but this method of signalling has become well known and developed under the auspices of Signor Marconi, who has succeeded in telegraphing by its means across the sea over distances up to twenty or thirty miles.

[O. L.]

Friday, March 10, 1899.

THE HON. SIR JAMES STIRLING, M.A. LL.D., Vice-President,  
in the Chair.

PROFESSOR H. L. CALLENDAR, M.A. F.R.S.

*Measuring Extreme Temperatures.*

THE measurement of extreme temperatures is a subject of great theoretical interest, especially in connection with the determination of the laws of radiation and of chemical dissociation and combination. The temperature in each case is the factor of paramount importance, and without means of measuring the temperature there is no possibility of formulating any rational theories. The subject possesses, in addition, a powerful fascination for the experimentalist, on account of the difficulty of the observations involved, and of the extremely conflicting nature of the results obtained by different observers and different methods of research.

Attempts have frequently been made to estimate the temperatures of the electric arc and of the sun, which may be taken as examples of the most extreme temperatures known to science, and afford an illustration of the difficulties to be encountered, and of the methods available for attacking these problems. A brief consideration and comparison of the results will also serve to explain the causes of the remarkable discrepancies existing in the estimates of such temperatures by different observers and different methods.

In the case of the sun it is at once obvious that no terrestrial thermometer can possibly be directly applied. The only available method is (1) to measure the intensity of the solar radiation, and (2) to endeavour to deduce the temperature by determining the law of radiation at high temperatures. The measurement of the intensity of the solar radiation is in itself a sufficiently intricate problem, containing many elements of doubt and difficulty; but by far the greatest source of uncertainty lies in the solution of the second part of the investigation, the determination of the law of radiation. The origin of the discrepancies thus imported into the results may be summed up in the word "Extrapolation."

The method of investigation necessarily consists in taking a series of observations at temperatures within the laboratory range of thermometry, from which to calculate an empirical formula representing as closely as possible the results of experiment. It is then assumed that the formula may be "extrapolated," or used to estimate the temperature of a radiating source of known intensity *beyond the range* of the observations on which it was founded. This is a perfectly

justifiable method, and may lead to very good results if the empirical law happens to be correct; but if the formula happens to be unsuitable, it may lead to the most remarkable conclusions.

The curves shown in Fig. 1 illustrate some of the typical formulæ which have either been proposed for the law of radiation, or been

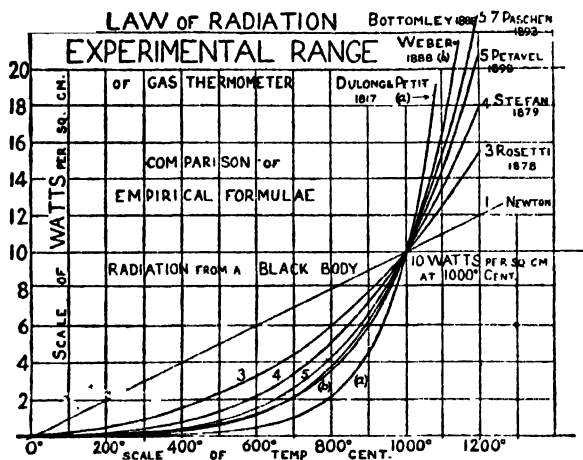


FIG. 1.—Formulæ of Radiation. Experimental range.

deduced from the results of modern experiments over the experimental range of the gas-thermometer, extending to  $1200^{\circ}\text{C}$ ., to which trustworthy determinations of temperature on the theoretical scale are at present restricted. In order to obtain a comparison of the formulæ themselves, apart from other issues, the results of different observers are reduced to a common hypothetical value, 10 watts per square centimetre, for the radiation from a black body at  $1000^{\circ}\text{C}$ .

Excluding the law of Newton, which applies only to small differences of temperature, and also the law of Dulong and Petit, which was founded on observations over a very limited range with mercury thermometers, and is obviously inapplicable at high temperatures, there is a certain family resemblance between the remaining curves; but the differences between them are still so considerable that, if sufficiently accurate measurements of temperature were available, it should be possible to decide with certainty which of the formulæ was the most correct. A fairly close agreement is seen to obtain between the formula proposed by Weber and the curves representing the results of the recent experiments of Bottomley, Paschen and Petavel. But, on the other hand, there is strong evidence, both experimental and theoretical, in favour of the fourth power law proposed by Stefan, which differs materially from that of Weber; and many supporters may be found, especially among astronomers, for the very different formula of Rosetti.

The importance of choosing a correct formula is most easily realised by reference to Fig. 2, which represents the results of extrapolation as applied to deducing the probable temperature of the sun. On the scale of Fig. 2, the dimensions of the experimental range of Fig. 1 are reduced to the thickness of the line at the lower left-hand corner of the diagram. The line at the top represents the intensity of solar radiation, which is taken at 10,000 watts per square centimetre in round numbers. The points at which the various curves meet this line show the corresponding values of the solar temperature.

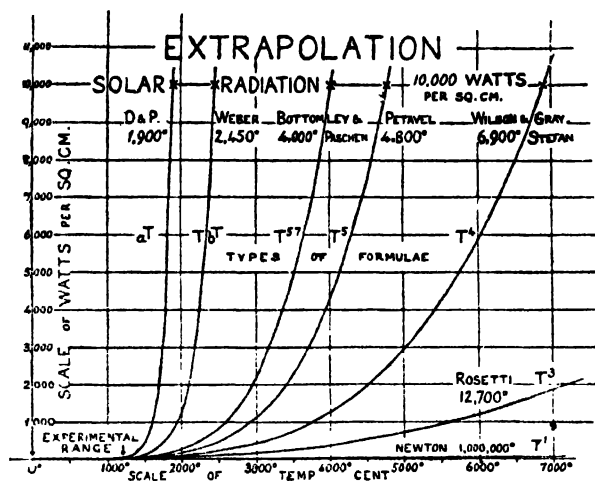


FIG. 2.—Temperature of the Sun by Extrapolation.

The estimates of one million degrees and upwards, which were current in many of the older books on astronomy, were deduced from the law of Newton, and are obviously out of the question. The celebrated formula of Dulong and Petit gives results between 1500° and 2000° C., according to the data assumed, and evidently errs too much in the other direction. At the same time, it must be observed that the recent formula of Weber gives a result which is very little higher. Paschen considered that his results lent support to Weber's formula, and disagreed entirely with Bottomley's. But, according to the writer's reductions, they agree very closely with Bottomley's, and are best represented by the formula  $ET^{1/7}$ . The experiments of Petavel agree most nearly with a fifth power law. On the other hand, the experiments of Wilson and Gray, in which the temperature was measured by the *expansion* of a platinum strip, instead of by the increase of its electrical resistance, appear to be in exact confirmation of the fourth power law of Stefan, and give a much higher result for the solar temperature. The formula of Rosetti is approximately  $\frac{1}{2}$

third power law at high temperatures, and would not be admitted as probable, at least by physicists, at the present time.

The various formulæ above mentioned, together with the methods employed and the results deduced, are summarised in the following table:—

TABLE I.—LAW OF RADIATION.

Observers and date.	Temperature measured by	Radiation observed by	Formula proposed.	Solar temp. deduced.
Dulong and Petit (1817)	Mercury thermometer	Rate of cooling in vac.	$E_1 1 \cdot 0077^{\tau}$	$^{\circ}\text{C.}$ 1900
Rosetti (1878) ..	Mercury thermometer	Thermopile	$E_2 T^3$ (nearly)	12,700
Stefan (1878) ..	No experiments made.	Sb-Bi	$E_3 T^4$	6900
Schleiermacher (1885)	Platinum resistance	Heat loss	$E_4 T^4$	6900
Weber (1888) ..	No experiments made.	$\text{C}^2\text{R}$ in vac.	$E_2 T 1 \cdot 00043^{\tau}$	2450
Bottomley (1888) ..	Platinum resistance	Heat loss	$E_5 T^{2 \cdot 7} *$	4000
Paschen (1893) ..	Thermo-couple	$\text{C}^2\text{R}$ in vac.	$E_6 T^{5 \cdot 7} *$	4000
Wilson and Gray (1897)	Pt-Pt Rh	Bolometer	$E_4 T^4$	6900
Petavel (1898) ..	Platinum expansion	Radio-micrometer	$E_5 T^3 *$	4800
	Platinum resistance	Bolometer		

\* Formulæ deduced by the writer from the observations.

The foregoing table is not intended to be exhaustive, but merely as a comparison of typical formulæ, reduced to a common standard. It does not contain the results of photometric investigations.

The conclusion to be derived from the above illustrations appears to be, that in order to arrive at any certain knowledge with regard to the law of radiation, and the measurement of such extreme temperatures as those of the arc, and of the sun, the first step must be to secure a higher order of accuracy in the determination of the highest temperatures which can be observed and measured in the laboratory with material thermometers. There are other difficulties which are peculiar to the determination of the law of radiation, but we are at present concerned primarily with those relating to the measurement of temperature.

There are two comparatively independent lines along which research may proceed with advantage at the present time: (1) The direct comparison of different arbitrary methods; (2) the extension of the range of the gas-thermometer.

In order to secure consistency of statement and the reduction of the results of different observers to a common standard, it is in the first place desirable that the various methods available at the present time for the measurement of high temperatures in the laboratory should be *directly compared inter se*, through the greatest possible range. It is

the custom at present for different observers to reduce their results *indirectly* to the scale of the gas-thermometer by reference to certain assumed values of the boiling and freezing points of various substances. They generally assume different values for these fixed points, and adopt different methods of calibration, which are undoubtedly responsible for many of the discrepancies at present existing.

To take an illustration from the experiments already quoted, the remarkable discrepancy between the experiments of Bottomley, Paschen and Petavel, on the one hand, and those of Wilson and Gray and Schleiermacher, on the other, in the determination of the intensity of radiation from polished platinum, may be traced primarily to differences in the methods of measurement adopted. Bottomley and Petavel measured the electrical resistance of the radiating wire itself, and deduced the temperature by the usual formula for the platinum scale. Paschen calibrated his thermo-couple by reference to numerous fusing and boiling points. Wilson and Gray adopted the maldometer methods based on the expansion of platinum, which they found to be uniform. The vacuum in Schleiermacher's experiments could not be measured, and was probably vitiated by gas evolved from the heated platinum.

These and similar discrepancies might be in a great measure removed, so far as they depend on the measurement of temperature, by the direct comparison of the various methods of measurement. The "platinum" methods are among the most important and the most easily comparable by direct experiment. These methods are founded on the characteristic stability and infusibility of the metals of the platinum group, properties which are accompanied by an even more remarkable degree of constancy in their less obvious electrical attributes. The two older methods, based on (1) the expansion and (2) the specific heat of platinum, are of comparatively limited application, but have given very good results in the able hands of Joly and Violle. The more modern electrical methods have the advantage of much wider applicability and convenience. They are of two distinct kinds: (3) the thermo-electric method, represented by the Pt-Pd thermo-couple of Becquerel the Pt-Ir thermo-couple of Barus, and the Pt-Rh thermo-couple of Le Chatelier, and (4) the platinum resistance pyrometer of Siemens. The third method has been naturalised in this country, and brought to great perfection by the work of Sir William Roberts-Austen. The fourth method was that adopted by Bottomley, Schleiermacher, and Petavel in the experiments above mentioned, and has been applied with great success by Heycock and Neville at high temperatures, and by Dewar and Fleming at the other extremity of the scale.

The usual or indirect comparison of the foregoing methods by means of the fusing points of various metals is illustrated in the annexed table, which contains several of the most recent results. The numbers given in brackets are now published for the first time, and should be regarded as preliminary.



TABLE II.—FUSING POINTS BY "PLATINUM" METHODS.

Method.	Observers.	Silver.	Gold.	Copper.	Palladium.	Platinum.
(1) Expansion .. ..	C. & E. (1899) ..	(945)	(1061)	(1085)	(1640)	(1980°)
(2) Spec. heat .. ..	Violle (1879) ..	957°	1045°	1054°	1500°	1775°
(3) Thermo-couples	Becquerel (1863)	960°	1092°	1221°	..	..
	Barus (1892) ..	985°	1093°	1097°	1643°	1855°
	" (1894) ..	986°	1091°	1096°	1585°	1757°
	Holborn & Wien (1895) .. ..	968°	1072°	1082°	1587°	1780°
	H. & N. (1895) ..	961°	1061°	1082°	..	..
(4) Resistance .. {	C. & E. (1899) ..	..	..	..	(1550)	(1820)

The results above given for the expansion method (1) were obtained by assuming the expansion to be uniform, and taking the F.P. of gold as 1061°. The results of Violle by the specific heat method (2) were deduced by assuming a linear formula for the specific heat of platinum. The discrepancies of the various results obtained by the thermo-electric method (3) are partly due to errors of observation, and partly to extrapolation, i.e. to differences in the formulae of reduction. The high value found by Becquerel for the F.P. of copper as compared with gold and silver is probably to be explained by the use of a much thicker wire in the case of copper. The very accurate and consistent experiments of Heycock and Neville leave little doubt that the F.P. of pure copper is at least 20° above that of gold. The much smaller difference of 4° to 5°, given by Barus, may possibly be explained by contamination with oxygen or other impurity. In the case of silver and gold, Messrs. Holborn and Wien adopted the Becquerel method of observing the fusion of fine wires. In the case of copper, they adopted the much more accurate method of observing the freezing point of a large mass of metal in a crucible, which had been employed by the writer in 1892, and was used by Heycock and Neville throughout their researches. The Becquerel method is very liable to give results which are too high.

The determination of the higher fusing points of palladium and platinum is necessarily attended with greater uncertainty because it involves extrapolation, and is therefore more dependent on the particular formula of reduction assumed, in addition to the experimental difficulties of the higher temperatures. Considering all the obstacles to be encountered, it would be unreasonable to expect such different methods to give any closer agreement at these points.

Whatever the origin of these discrepancies, there can be no question that they greatly retard the progress of research and discovery at high temperatures. With the object of helping to remove these obstacles, the writer has recently been engaged, in conjunction

with Mr. Eumorfopoulos, in a direct comparison of methods (1), (3) and (4), which are simplest and most generally applicable. The advantages of the direct method of comparison are very great. (1) The comparison may be extended continuously throughout the scale, and is not confined to a few arbitrary selected points. (2) It is easy to apply the electric method of heating, which is of all methods the most easily regulated. (3) It is easy to arrange the experiments in such a way that there can be no question of difference of temperature between the thermometers under comparison, which is the most insidious source of error in high temperature measurement.

In the comparison of the scale of the expansion of platinum (1), with that of the platinum resistance thermometer (4), it is simply necessary to observe simultaneously the expansion and the electric resistance of a platinum strip, tube or wire maintained at a steady temperature by means of an electric current. The expansion may be measured, as in the maldrometer of Joly, by means of a micrometer screw; but for lecture purposes it is preferable to adopt the method of the optical lever employed by Laplace in his experiments on expansion a century ago. By employing a direct-reading ohmmeter to indicate the changes of electrical resistance, it is thus possible to exhibit the difference between the two methods by the simultaneous advance of two spots of light on a single scale. If the two instruments are adjusted to read correctly at  $0^{\circ}$  and  $1000^{\circ}$  C., the resistance thermometer will be in advance at temperatures below  $1000^{\circ}$ , but will lag behind at higher temperatures, because the rate of expansion increases as the temperature rises, whereas the rate of change of resistance diminishes. As the result of these experiments, it appears that the two scales (1) and (4) differ from that of the gas-thermometer to a nearly equal extent, but in opposite directions.

The resistance of platinum at its melting point is more than six times as great as at  $0^{\circ}$  C., whereas the whole expansion amounts to only one-fiftieth part of the length. The electrical method is for this reason by far the most accurate and sensitive. It also possesses in a very striking degree the merit of pliability and adaptability to the needs of each particular problem. For this reason the scale of the platinum resistance thermometer has come to be regarded as the platinum scale *par excellence*, and has been adopted as the standard of reference in many recent researches.

As an illustration of the facility of applying this method, the determination of the fusing point of platinum on the platinum scale may be taken. This is a difficult experiment to perform by any other method. In performing the experiment by the measurement of the electrical resistance, it suffices to take a fine wire of which the electrical constants are accurately known, and to raise it gradually to its melting point by steadily increasing the current. The observation of the resistance of the central portions of the wire at the moment of fusion gives directly the temperature required on the platinum scale. In attempting to perform the same experiment by the expansion

method, we are met by the difficulty that the platinum begins to soften and stretch at a temperature considerably below its melting point. Owing to the smallness of the expansion, a very slight viscous extension produces a relatively large error. In the resistance method it is not necessary to subject the wire to tension, and a small strain would in any case produce an inappreciable error on account of the very large increase of resistance with temperature. To obtain an equal degree of accuracy by the calorimetric method (2), or the thermo-electric method (3), it is necessary to use a furnace in which relatively large quantities of platinum can be melted. This has been done by Violle for method (2), and by Barnes and Holborn and Wien for method (3). The latter used a linear formula for extrapolation, although their gas-thermometer experiments appeared to indicate a cubic formula for temperatures below  $1200^{\circ}\text{C}$ .

The temperature of the melting point of platinum on the platinum scale by the resistance method (4) is approximately  $pt = 1350^{\circ}$ , and varies but slightly for different specimens of platinum. The result, when reduced to the scale of the gas-thermometer by assuming that the rate of increase of resistance diminishes uniformly with rise of temperature (according to the usual formula of platinum thermometry, which has been verified with great care at moderate temperatures), gives a temperature of  $1820^{\circ}\text{C}$ . on the scale of the gas-thermometer. It is not improbable that platinum may deviate slightly from this formula at the extreme limit of the scale in the close neighbourhood of its melting point, but the evidence for this result is at least as good as that obtainable by any of the other methods. The observations are very easy and accurate as compared with the calorimetric method, and it is not necessary to make any arbitrary assumptions with regard to the formula of reduction, as in the case of the thermo-electric method.

As the accuracy of this formula has recently been called in question, on what appears to be insufficient grounds, by certain German and French observers, it is the more interesting at the present time to show that it leads to a result which cannot be regarded as improbable at the extreme limit of the scale. A different formula has recently been employed by Holborn and Wien, and supported by Dickson (*Phil. Mag.*, December 1897). The writer has already given reasons (*Phil. Mag.*, February 1899) for regarding this formula as inferior to the original, of which, however, it is a very close imitation. The above observations on the melting point of platinum, if reduced by Dickson's formula, would give a result  $t = 1636^{\circ}\text{C}$ ., which appears to be undoubtedly too low as compared with the results of other methods, however great the margin of uncertainty we are prepared to admit in these difficult and debatable regions of temperature measurement.

It should be observed that the results of Violle by method (2) are consistently lower than those given by the resistance method in the case of silver, gold and copper. We should, therefore, expect a

difference in the same direction at the F.P. of Pt as found by method (4), and not a difference in the opposite direction as given by the thermo-electric method, on the arbitrary assumption of a different type of formula for extrapolation at high temperatures. It is a matter of some interest that the assumption of linear formulæ for both the specific heat and the rate of change of resistance, should lead to results so nearly consistent over so wide a range of temperature in the case of platinum.

The chief difficulty and uncertainty encountered by Paschen in his experiments on radiation, was that of arranging the thermo-couple so as to be at the same temperature as the radiating strip of platinum. It is better for this reason to measure the temperature of the strip itself by means of its electrical resistance, the method adopted by Schleiermacher, Bottomley and Petavel. The same difficulty occurs in the direct comparison of the scales of the thermo-couple and the platinum-resistance thermometer. The simplest method of avoiding this objection appears to be that recently adopted by the writer, of enclosing the thermo-couple completely in a thin tube of platinum, which itself forms the resistance thermometer. There can be no question of difference of temperature between the two, and the same tube may serve simultaneously for the expansion method and as a radiating source for bolometric investigation of the law of radiation. The uniformity of temperature throughout the length of the tube can be tested at any time by means of potential leads, or by shifting the thermo-couple to different positions along its length. The method of electric heating is employed, and the central portion only of the tube is utilised in the comparison.

The methods of measurement, so far as considered, are in a certain sense *arbitrary* in so far as they depend on extrapolation of empirical formulæ. If all these methods could be reduced by direct comparison to perfect agreement with each other, a definite scale of temperature would be attained to which all measurements could be referred, and which would leave nothing to be desired from a purely practical point of view. It is probable that this scale would not differ much from the theoretical or absolute scale of temperature. For theoretical investigations, however—without which no true scientific advance can be made—it is a matter of such fundamental importance to refer every measurement to the absolute scale, that no opportunity should be neglected of extending the possible range of accurate observation with the gas-thermometer, because this instrument affords at present the closest approximation to the absolute or theoretical scale. A consideration of the difficulties of the methods of gas-thermometry at present in use will lead naturally to the best methods of extending the range and accuracy of the instrument.

In the ordinary method of gas-thermometry a *bulb* containing the gas is exposed to the temperature to be measured, and the observation consists in determining either the expansion of volume or the increase of pressure of the gas. The principle is very similar to that of the

ordinary liquid in glass thermometers, but the apparatus is more cumbersome and difficult to use on account of the necessity of observing both the volume and the pressure of the gas. This method is very accurate at moderate temperatures, but the difficulties increase very rapidly above  $1000^{\circ}\text{C}$ . Above  $1200^{\circ}\text{C}$ ., it is doubtful whether such measurements are of any greater value than those obtained by extrapolation. Apart from the difficulty (which is common to nearly all methods at high temperatures) of maintaining a uniform and steady temperature, the bulb-method of gas-thermometry is liable to the following special sources of error:—

- (1) Changes in volume of the bulb.
- (2) Leakage and porosity.
- (3) Occlusion or dissociation.

In order to investigate these sources of error a special form of porcelain air-thermometer (Fig. 3) was designed by the writer, and was constructed in Paris, in December 1886, under the supervision of

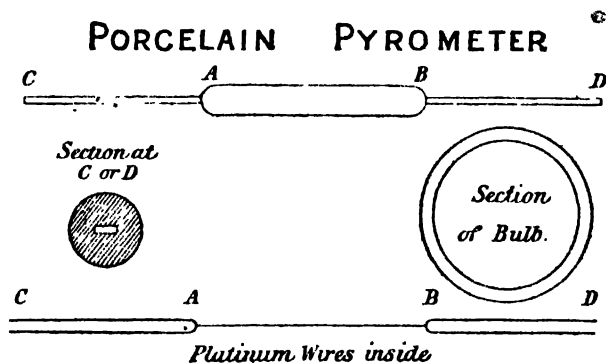


FIG. 3.

W. N. Shaw, F.R.S., of Emmanuel College, Cambridge. A figure and description of this instrument were published in the *Phil. Trans. A.*, 1887. The same form has since been adopted by MM. Holborn and Wien in their experiments on the measurement of high temperatures at the Reichsanstalt. Thick tubes of 3 sq. mm. cross section, marked *AC*, *BD* in Fig. 3, were connected at each end of the cylindrical bulb *BA*. The length *CD* could be directly observed at any time with reading microscopes, and the linear expansion of the bulb could be deduced. The volume of the bulb could also be gauged at any time with air, and the mean temperatures of the separate portions *AB*, *AC*, *BD*, could be determined by means of platinum wires extending along the axis of the instrument. This was a more essential part of the apparatus, as the wires afforded a means of accurately reproducing any given set of conditions, and of testing the performance of the

gas-thermometer at high temperatures in respect of all the various sources of error above mentioned. (1) It was observed that the volume of the bulb underwent continuous changes, chiefly in the direction of contraction, and that the shrinkage was not symmetrical, being apparently greater in the circumference than in the length of the cylinder. (2) To prevent leakage, and to close the pores of the material, it is necessary to have the porcelain bulb glazed both inside and out. The glaze becomes sticky, and begins to run at a temperature below  $1200^{\circ}\text{C.}$ , and the bulb begins to yield slightly and continuously to pressure above this point. (3) With some gases there appear to be slight traces of chemical action or occlusion of the gas by the walls of the bulb at high temperatures. It is for this reason preferable to use the inert gases nitrogen or argon as the thermometric material. In any case, the limit of high temperature measurement would be reached when either the gas, or the material of the bulb, began to dissociate or decompose. Deville and Troost, employing  $\text{CO}_2$  for filling the porcelain bulb, found the temperature of the B.P. of zinc nearly  $150^{\circ}$  higher than with air or hydrogen. This they attributed to a partial dissociation of the  $\text{CO}_2$  at the temperature as low as  $930^{\circ}\text{C.}$  Some experiments made by the writer appeared, however, to indicate that the effect was due to chemical action between the gas and the porcelain.

For these and other reasons it appears very doubtful whether any improvement or extension of range can be expected from the use of glazed porcelain. If an attempt is made to employ any of the more refractory kinds of fire-clay, there is the difficulty of finding a suitable glaze, and of eliminating leakage and porosity. The writer suggested the use of bulbs of fused silica some years ago (Proc. Iron and Steel Institute, 1892), and endeavoured to get such bulbs constructed, but without success. This material possesses many of the requisite qualities, but is for this very reason extremely difficult to work. Metallic bulbs of platinum or platinum-iridium are by far the most perfect in respect of constancy of volume, regularity of expansion, and facility of accurate construction; but unfortunately, as Deville and Troost showed, they have such an inveterate tendency for occluding or dissolving gases at high temperatures, that the use of metallic bulbs has been practically discontinued, in spite of their obvious advantages in other respects.

After making many vain experiments, the writer was forced to the conclusion that the ordinary bulb-methods did not promise any satisfactory solution of the problem of extending the range of the gas-thermometer, and that it was necessary to attempt a radically new departure. The optical method, depending on the measurement of the refractivity of a gas at high temperatures, and the acoustical method, depending on the observation of the wave-length of sound, although of great theoretical interest, did not appear to promise sufficient delicacy of measurement or facility of practical application. Experiments were therefore made on the methods of effusion and

transpiration, which had been occasionally suggested by previous writers, but have not as yet (so far as the author is aware) been practically investigated as a means of measuring temperature on the absolute scale. The method of effusion consists in observing the resistance to the efflux of gas through a small hole or orifice in a thin plate. In the method of transpiration the gas is made to pass through a fine tube instead of a small orifice, and the resistance to its passage is observed in a similar manner. These methods may be called "resistance-methods" to distinguish them from the ordinary or "bulb-methods" of pyrometry. They are closely analogous to the now familiar resistance-method of electrical pyrometry, and possess many of the advantages of that method in point of delicacy and facility of application. One very obvious and material advantage, especially for high temperature work, is the smallness and sensitiveness of the instrument as compared with the bulb of an ordinary gas-thermometer. But the most important point of difference, which led the writer to the adoption of these methods, is that the measurements are practically unaffected by occlusion or evolution of gas by the material of the tubes. There is a *continuous* flow of gas through the apparatus. This flow is very large in proportion to any possible leakage, and it is therefore possible to employ platinum tubes with perfect safety.

The method of effusion may be very simply illustrated by means of a fine hole in the side of a large and thin platinum tube which is heated by an electric current. The current of air is heated in its passage through the tube before it effuses through the orifice. The heated air expands in volume, and the resistance to effusion is increased in proportion to the temperature to which the air is heated. The increase of resistance may be shown by means of a gas-current indicator or "rheoscope," which consists of a delicately suspended vane deflected by a current of gas. A mirror is attached to the vane, and the deflection is measured by the motion of a spot of light reflected on to a scale, exactly as in the case of the mirror galvanometer when used for indicating changes of electrical resistance. As a standard of comparison, to show the changes of temperature of the tube, the changes of electrical resistance of the same tube are simultaneously shown by means of a suitable ohmmeter.

The method of effusion is a beautifully simple method, and gives a nearly uniform scale; but it has two disadvantages, which it shares with the thermo-electric method of measurement. (1) It necessarily measures temperature at a point, namely at the point of effusion, and cannot be easily arranged to give the mean temperature throughout a space. (2) It is difficult to make the effusion resistance sufficiently large for purposes of accurate measurement. A large resistance means a very fine hole, and it is not easy to satisfy the theoretical conditions of the problem with sufficient accuracy and eliminate the effects of viscosity.

The method of transpiration is more complicated, and does not

give so uniform a scale, or so simple a formula. It has the great advantage, however, that the theoretical conditions of flow may be realised with unlimited accuracy, and that the transpiration resistance can be measured with a degree of precision very little, if at all, inferior to the corresponding electrical measurement.

The complication of the transpiration problem arises from the fact that the flow depends on the increase of the viscosity of the gas, as well as on its expansion. The viscosity of liquids in general decreases very considerably with rise of temperature. That of water, for instance, is six times less at the boiling point than at the freezing point. If the viscosity of gases diminished in a similar manner, it might happen that the transpiration resistance would decrease with rise of temperature. Maxwell was the first to give a theoretical explanation of the behaviour of gases in this respect. On certain simple kinetic assumptions, he showed that the viscosity should increase in direct proportion to the absolute temperature. Since the expansion follows the same law, the transpiration resistance on Maxwell's hypothesis should increase in proportion to the square of the temperature. This would give a fairly simple formula, and would make the transpiration thermometer a very sensitive instrument, but the scale would be very far from uniform. Maxwell made some experiments on the temperature variation of the viscosity between 0° and 100° C., which appeared to give support to his mathematical assumptions; but his apparatus did not happen to be of a very suitable type for temperature measurement, and it is clear that he did not regard this part of his experimental work with great confidence.

The question of the viscosity of gases was next attacked with great vigour in Germany by a number of different physicists. They ultimately succeeded in proving that the law was not quite so simple as Maxwell had supposed, and that the rate of increase of viscosity was less than that of volume. A summary of some of the principal results obtained, over the range 0° to 100° C., is given in the following

TABLE III.—VARIATION OF VISCOSITY  $\nu$  WITH TEMPERATURE  $T$ .  
FORMULA,  $\nu/\nu_0 = (T/T_0)^n$ .

Observers.	Dates	Values of Index $n$ (0° to 100° C.)			
		Air.	O <sub>2</sub> .	H <sub>2</sub> .	CO <sub>2</sub> .
Maxwell .. .. .	1866	1·000	—	—	
Meyer .. .. .	1873	61 — ·83	—	—	
Puluj .. .. .	1874	47 — ·65	—	—	
Obermeyer .. ..	1875	·76	·80	·70	·94
Wiedemann .. ..	1876	·73	—	—	·93
Warburg .. .. .	1876	74 — ·77	—	·63	
" and Kundt	1876	·72	—	·69	
Holman .. .. .	1876	74 — ·80	—	—	



table, in which the rate of increase is expressed by finding the power  $n$  of the absolute temperature  $T$  to which the viscosity is most nearly proportional. The most concordant results were obtained by the method of transpiration, and gave an average of  $\cdot 76$  for the index  $n$  in the case of air. The more condensable gases gave larger values for the rate of increase, but the value for hydrogen appeared to be smaller.

It will be observed that the results are not very concordant, but the experiments are much more difficult and liable to error than might be supposed. The most accurate method was that employed by Holman, but even in this case the margin of uncertainty is considerable. It would evidently be impossible to employ the method of transpiration to any advantage for the determination of temperature, unless a far higher order of accuracy could be easily attained. After repeating the majority of the more promising methods in detail, including the original method of Maxwell, the writer came to the conclusion that they were entirely unsuitable for the purposes of thermometry, and would have abandoned the attempt entirely if he had not, fortunately succeeded in finding a more perfect way.

In studying the flow of electricity through conductors, which is in many respects analogous to that of a fluid through a fine tube, electricians have been compelled, from the intangible nature of the fluid with which they work, to elaborate the most delicate and powerful methods of investigation. One of the most useful of these methods is generally known as the Wheatstone-bridge method, and is used for measuring the resistance of a conductor to the passage of an electric current. The method is equally applicable and equally exact for determining the resistance of a fine tube to the passage of a gas. The writer was already very familiar with the application of this method in all its refinement of detail to electrical resistance thermometry. The suggestion for applying it to the closely analogous problem of transpiration was supplied by the researches of W. N. Shaw, F.R.S., who had already applied it, in connection with certain experiments on ventilation, to the effusion of air through large orifices at ordinary temperatures.

The apparatus used by Shaw (described in the Proc. Roy. Soc., vol. xlvii., 1890) consisted of boxes to represent rooms, with apertures about half a square inch in area to represent ventilators. Two of these apertures were made in the form of adjustable slits. The circulation of air through two rooms in parallel was maintained by a gas burner, and the slits were adjusted to make the pressure in the two rooms the same, as indicated by the absence of flow in a connecting tube, containing a pivoted needle and vane as a current detector. The balance was shown to be independent of the air-current when that was varied from one to four cubic feet per minute. The effusion resistance of an aperture was also verified to be approximately proportional to the square of the reciprocal of the area, with apertures of similar shape. This method of investigation was admirably adapted

to problems in ventilation, in which the phenomena depend mainly on effusion through relatively large apertures. It would, however, be difficult to adapt to the problem of temperature measurement. It would not be easy to make an aperture which could be continuously varied without changing its shape, and at the same time to measure the change of area with sufficient accuracy, if the area were small enough to prevent appreciable cooling of the thermometer by the current of air flowing through it. There is also the disadvantage that the pressure-difference varies as the square of the current; so that, if very small currents are used, the effects of viscosity become more important, and the balance ceases to be independent of the current, unless everything is symmetrical and at the same temperature in corresponding parts.

For these reasons it seems preferable, in applying the Wheatstone-bridge method to air-currents, to employ fine tubes as resistances, and to eliminate the effects of effusion as completely as possible, at least in the resistance-measuring part of the apparatus. With transpiration resistances the current is directly proportional to the pressure difference, the electrical analogy is much closer, and the theoretical conditions can be very accurately realised.

The Wheatstone-bridge method of measurement proved to be so exact, and so perfectly adapted to the problem of transpiration thermometry, that, after some preliminary experiments, the writer had a very elaborate apparatus constructed, in the year 1893, which was in every detail the exact analogue of an electrical resistance thermometer. The fine wire resistances of the electrical apparatus, in terms of which the change of resistance of the thermometer is measured, are replaced in the transpiration box by a graduated series of fine tubes, which can be short-circuited by means of taps of relatively large bore, corresponding to the plugs of negligible resistance in the electrical resistance box. The galvanometer is replaced by a rheoscope, constructed after a pattern devised by Joule for a different purpose, which can be made to rival in delicacy the best modern electrical instruments. The pyrometer itself consists of a fine tube of platinum instead of a wire, and is fitted with "compensating leads" to correspond with those of the electrical instrument. All the detail of the methods of observation and calibration are faithfully copied from the electrical apparatus, and the results, so far as the measurement of transpiration resistance is concerned, are equally satisfactory.

Fig. 4 is a diagram of a working model of the transpiration balance, which was exhibited at the lecture. This model has a vertical needle for index, and a pivoted mica vane, which is deflected when a current flows through the bridge piece. It is constructed to work on the ordinary lighting-gas pressure, and to give its maximum deflection for a 10 per cent. change of resistance with the gas about half off. With all the taps off, the resistances on either side are equal, and there is no deflection. In the diagram the balance is supposed to have been disturbed by opening one of the taps. The apparatus

actually used for temperature measurement has sixteen taps and a mirror rheoscope, and is a thousand times more sensitive.

In order to apply the method to the measurement of extreme temperatures, it is not sufficient to be able to measure resistance. It is also necessary to determine the law of the variation of viscosity with temperature. Here, again, recourse must be had to the method of extrapolation. Fortunately, in the present instance, the temperature can be measured through a very wide range, and the range of extrapolation, being limited by the melting point of platinum, is not

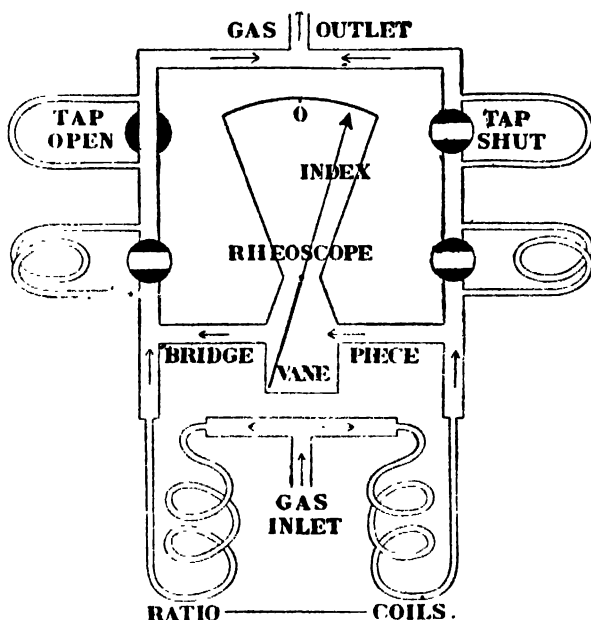


FIG. 4.—Diagram of Transpiration Balance.

very great in comparison. It should be possible, therefore, by sufficiently varying the conditions of the experiments, and by comparing the behaviour of different gases throughout the whole range of temperature, to arrive at a very fair degree of certainty with regard to the essential nature of the phenomenon. Owing to want of leisure for the work, the author's experiments have not as yet extended over a sufficient range of temperature, except in the case of air, to warrant the publication of any general conclusions with regard to the law of variation of viscosity, or of any results at high temperatures obtained by the method of extrapolation. It may be stated, however, that the formula above quoted, according to which the viscosity varies as some

power  $n$  of the temperature, though fairly exact over a moderate range of temperature, fails entirely when tested at higher points. The results of Obermayer appear to be the most accurate for the different gases between  $0^{\circ}$  and  $100^{\circ}$  C., but if the same formula is retained, the value of the index  $n$  diminishes as the temperature is raised. Taking the average value between  $0^{\circ}$  and  $100^{\circ}$  for air as being 0.76, the value falls to 0.70 between  $100^{\circ}$  and  $450^{\circ}$ . A result of this nature was found by Wiedemann, but the rate of diminution which he gives appears to be far too great. He gives, for instance, the value  $n = 0.67$  for air between  $0^{\circ}$  and  $184^{\circ}$ , which implies a rate of diminution of the index many times greater than that which actually occurs. It would be very difficult by the method which he employed to make sure of *any* deviation whatever from the formula over so small a range, and since the error of his determination is much greater than that of the formula, he can hardly be said to have disproved the index law.

The problem is seriously complicated by the failure of the simple formula; but since the measurements are capable of great exactitude, and since it is possible to obtain many independent checks by comparing the results of the two methods of effusion and transpiration, and also by examining the behaviour of different gases, the author is confident of ultimate success. The method of experiment here described has already led to many promising and interesting results, and it is probable that the complete solution of the problem when attained, besides leading to more accurate determinations of extreme temperatures, may also throw light on dissociation and on many other points which are at present obscure in the theory of gases.

[H. L. C.]

Friday, March 24, 1899.

SIR FREDERICK BRAMWELL, BART., D.C.L. LL.D. F.R.S.,  
Honorary Secretary and Vice-President, in the Chair.

The Right Hon. LORD RAYLEIGH, M.A. D.C.L. LL.D. F.R.S. M.R.I.,  
Professor of Natural Philosophy, R.I.

*Transparency and Opacity.*

ONE kind of opacity is due to absorption; but the lecture dealt rather with that deficiency of transparency which depends upon irregular reflections and refractions. One of the best examples is that met with in Christiansen's experiment. Powdered glass, all from one piece and free from dirt, is placed in a bottle with parallel flat sides. In this state it is quite opaque; but if the interstices between the fragments are filled up with a liquid mixture of bisulphide of carbon and benzole, carefully adjusted so as to be of equal refractivity with the glass, the mass becomes optically homogeneous, and therefore transparent. In consequence, however, of the different dispersive powers of the two substances, the adjustment is good for one part only of the spectrum, other parts being scattered in transmission much as if no liquid were employed, though, of course, in a less degree. The consequence is that a small source of light, backed preferably by a dark ground, is seen in its natural outlines but strongly coloured. The colour depends upon the precise composition of the liquid, and further varies with the temperature, a few degrees of warmth sufficing to cause a transition from red through yellow to green.

The lecturer had long been aware that the light regularly transmitted through a stratum from 15 to 20 mm. thick was of a high degree of purity, but it was only recently that he found to his astonishment, as the result of a more particular observation, that the range of refrangibility included was but two and a half times that embraced by the two D-lines. The poverty of general effect, when the darkness of the background is not attended to, was thus explained; for the highly monochromatic and accordingly attenuated light from the special source is then overlaid by diffused light of other colours.

More precise determinations of the range of light transmitted were subsequently effected with thinner strata of glass powder contained in cells formed of parallel glass. The cell may be placed between the prisms of the spectroscope and the object-glass of the collimator. With the above mentioned liquids a stratum 5 mm. thick transmitted, without appreciable disturbance, a range of the spectrum measured by 11.3 times the interval of the D's. In another cell of

the same thickness an effort was made to reduce the difference of dispersive powers. To this end the powder was of plate glass and the liquid oil of cedar-wood adjusted with a little bisulphide of carbon. The general transparency of this cell was the highest yet observed. When it was tested upon the spectrum, the range of refrangibility transmitted was estimated at 34 times the interval of the D's.

As regards the substitution of other transparent solid material for glass, the choice is restricted by the presumed necessity of avoiding appreciable double refraction. Common salt is singly refracting, but attempts to use it were not successful. Opaque patches always interfered. With the idea that these might be due to included mother liquor, the salt was heated to incipient redness, but with little advantage. Transparent rock-salt artificially broken may, however, be used with good effect, but there is some difficulty in preventing the approximately rectangular fragments from arranging themselves too closely.

The principle of evanescent refraction may also be applied to the spectroscope. Some twenty years ago, an instrument had been constructed upon this plan. Twelve  $90^\circ$  prisms of Chance's "dense flint" were cemented in a row upon a strip of glass (Fig. 1), and the whole was immersed in a liquid mixture of bisulphide of carbon with a little benzole. The dispersive power of the liquid exceeds that of the solid, and the difference amounts to about three-quarters of the

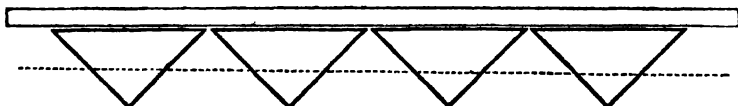


FIG. 1.

dispersive power of Chance's "extra dense flint." The resolving power of the latter glass is measured by the number of centimetres of available thickness, if we take the power required to resolve the D-lines as unity. The compound spectroscope had an available thickness of 12 inches or 30 cm., so that its theoretical resolving power (in the yellow region of the spectrum) would be about 22. With the aid of a reflector the prism could be used twice over, and then the resolving power is doubled.

One of the objections to a spectroscope depending upon bisulphide of carbon is the sensitiveness to temperature. In the ordinary arrangement of prisms the refracting edges are vortical. If, as often happens, the upper part of a fluid prism is warmer than the lower, the definition is ruined, one degree (Centigrade) of temperature making nine times as great a difference of refraction as a passage from  $D_1$  to  $D_2$ . The objection is to a great extent obviated by so mounting the compound prism that the refracting edges are *horizontal*, which of course entails a horizontal slit. The disturbance due to a stratified temperature is then largely compensated by a change of focus.

In the instrument above described the dispersive power is great—

the D-lines are seen widely separated with the naked eye—but the aperture is inconveniently small ( $\frac{1}{2}$ -inch). In the new instrument exhibited the prisms (supplied by Messrs. Watson) are larger, so that a line of ten prisms occupies 20 inches. Thus, while the resolving power is much greater, the dispersion is less than before.

In the course of the lecture the instrument was applied to show the duplicity of the reversed soda lines. The interval on the screen between the centres of the dark lines was about half an inch.

It is instructive to compare the action of the glass powder with that of the spectroscope. In the latter the disposition of the prisms is regular, and in passing from one edge of the beam to the other there is complete substitution of liquid for glass over the whole length. For one kind of light there is no relative retardation; and the resolving power depends upon the question of what change of wave length is required in order that its relative retardation may be altered from zero to the quarter wave length. All kinds of light for which the relative retardation is less than this remain mixed. In the case of the powder we have similar questions to consider. For one kind of light the medium is optically homogeneous, i.e. the retardation is the same along all rays. If we now suppose the quality of the light slightly varied, the retardation is no longer precisely the same along all rays; but if the variation from the mean falls short of the quarter wave length it is without importance, and the medium still behaves practically as if it were homogeneous. The difference between the action of the powder and that of the regular prisms in the spectroscope depends upon this, that in the latter there is complete substitution of glass for liquid along the extreme rays, while in the former the paths of all the rays lie partly through glass and partly through liquid in nearly the same proportions. The difference of retardations along various rays is thus a question of a deviation from an average.

It is true that we may imagine a relative distribution of glass and liquid that would more nearly assimilate the two cases. If, for example, the glass consisted of equal spheres resting against one another in cubic order, some rays might pass entirely through glass and others entirely through liquid, and then the quarter wave length of relative retardation would enter at the same total thickness in both cases. But such an arrangement would be highly unstable; and, if the spheres be packed in close order, the extreme relative retardation would be much less. The latter arrangement, for which exact results could readily be calculated, represents the glass powder more nearly than does the cubic order.

A simplified problem, in which the element of chance is retained, may be constructed by supposing the particles of glass replaced by thin parallel discs which are distributed entirely at random over a certain stratum. We may go further and imagine the discs limited to a particular plane. Each disc is supposed to exercise a minute retarding influence on the light which traverses it, and they are sup-

posed to be so numerous that it is improbable that a ray can pass the plane without encountering a large number. A certain number ( $m$ ) of encounters is more probable than any other, but if every ray encountered the same number of discs, the retardation would be uniform and lead to no disturbance.

It is a question of Probabilities to determine the chance of a prescribed number of encounters, or of a prescribed deviation from the mean. In the notation of the integral calculus the chance of the deviation from  $m$  lying between  $\pm r$  is \*

$$\frac{2}{\sqrt{\pi}} \int_0^r e^{-\tau^2} d\tau,$$

where  $\tau = r / \sqrt{(2m)}$ . This is equal to .84 when  $\tau = 1.0$ , or  $r = \sqrt{(2m)}$ ; so that the chance is comparatively small of a deviation from  $m$  exceeding  $\pm \sqrt{(2m)}$ .

To represent the glass powder occupying a stratum of 2 cm. thick, we may perhaps suppose that  $m = 72$ . There would thus be a moderate chance of a difference of retardations equal to, say, one-fifth of the extreme difference corresponding to a substitution of glass for liquid throughout the whole thickness. The range of wave lengths in the light regularly transmitted by the powder would thus be about five times the range of wave lengths still unseparated in a spectroscope of equal (2 cm.) thickness. Of course, no calculation of this kind can give more than a rough idea of the action of the powder, whose disposition, though partly a matter of chance, is also influenced by mechanical considerations; but it appears, at any rate, that the character of the light regularly transmitted by the powder is such as may reasonably be explained.

As regards the size of the grains of glass, it will be seen that as great or a greater degree of purity may be obtained in a given thickness from coarse grains as from fine ones, but the light not regularly transmitted is dispersed through smaller angles. Here again the comparison with the regularly disposed prisms of an actual spectroscope is useful.

At the close of the lecture the failure of transparency which arises from the presence of particles small compared to the wave length of light was discussed. The tints of the setting sun were illustrated by passing the light from the electric lamp through a liquid in which a precipitate of sulphur was slowly forming.† The lecturer gave reasons for his opinion that the blue of the sky is not wholly, or even principally, due to particles of foreign matter. The molecules of air themselves are competent to disperse a light not greatly inferior in brightness to that which we receive from the sky.

[R.]

\* See Phil. Mag. 1899, vol. xlvii. p. 251.

† Op. cit. 1881, vol. xii. p. 96.



Friday, May 5, 1899.

SIR FREDERICK BRAMWELL, BART., D.C.L. LL.D. F.R.S., Honorary  
Secretary and Vice-President, in the Chair.

WILLIAM JAMES RUSSELL, Esq., Ph.D. V.P.R.S. M.B.I.

*Pictures Produced on Photographic Plates in the Dark.*

I THINK I may fairly assume that every one in this theatre has had their photograph taken, and consequently must have some idea of the nature of the process employed. I have, therefore, only to add, with regard to what is not visible in the process of taking the picture, that the photographic plate is a piece of glass or such like body, coated on one side by an adhesive paste which is acted on by light, and acted on in a very remarkable manner. No visible change is produced, and the picture might remain latent for years, but place this acted-on plate in a solution, of, say pyrogallol, and the picture appears. The subsequent treatment of the plate with sodium hyposulphite is for another purpose, simply to prevent the continuance of the action when the plate is brought into the light. Now, what I purpose demonstrating to you to-night is that there are other ways of producing pictures on photographic plates than by acting on them by light, and that by these other means a latent picture is formed, which is rendered visible in precisely the same way as the light pictures are.

The substances which produce on a photographic plate these results so strongly resembling those produced by light, are, some of them, metallic, while others are of vegetable origin. At first it seemed very remarkable that bodies so different in character should act in the same way on the photographic plate. The following metals—magnesium, cadmium, zinc, nickel, aluminium, lead, bismuth, tin, cobalt, antimony—are all capable of acting on a photographic plate. Magnesium most strongly, antimony but feebly, and other metals can also act in the same way, but only to a very slight extent. The action in general is much slower than that of light, but under favourable conditions a picture may be produced in two or three seconds.

Zinc is nearly as active as magnesium or cadmium, and is the most convenient metal to experiment with. In its ordinary dull state it is without the power of acting on a photographic plate, but scratch it or scrape it, and it is easy to prove that the bright metal is active. I would say that all the pictures which I have to show you, by means of the lantern, are produced by the direct action of the metal,

or whatever the active body may be, on the photographic plate, and that they have not been intensified or touched up in any way. This first slide is the picture given by a piece of ordinary zinc which has been rubbed with some coarse sand-paper, and you see the picture of every scratch. Here is a piece of dull zinc on which some circles have been turned. It was exposed to the photographic plate for four hours at a temperature of  $55^{\circ}\text{C}$ . In the other cases, which are on a larger scale, a zinc stencil was polished and laid upon a photographic plate, and you see where the zinc was in contact with the plate much action has occurred. In another case a bright zinc plate was used, and a Japanese stencil interposed between it and the photographic plate, and a very strong and sharp picture is the result. The time required to produce these zinc pictures varies very much with the temperature. At ordinary temperature the exposure would have to be for about two days, but if the temperature was, say,  $55^{\circ}\text{C}$ ., then half to three-quarters of an hour might be sufficient. Temperatures higher than this cannot be used except for very short times, as the photographic plate would be damaged. Contact between the zinc and photographic plate is not necessary, as the action readily takes place through considerable distances. Obviously, however, as you increase the distance between object and plate, so you decrease the sharpness of the picture, as is shown by the following pictures, which were taken respectively at a distance of 1 mm. and 3 mm. from the scratched zinc surface. The appearance of the surfaces of different metals varies, and the following slides show the surface of a plate of bismuth, a plate of lead, and one of aluminium. On the next slide are the pictures produced by similar pieces of pure nickel and cobalt, and it clearly shows how much more active in this way nickel is than cobalt. Many alloys, such as pewter, fusible metal, brass, etc., are active bodies, and in the case of brass the amount of action which occurs is determined by the amount of zinc present. Thus you will see that a brass with 30 per cent. of zinc produces hardly any action on the photographic plate, but when 50 per cent. of zinc is present there is a fairly dark picture, and when as much as 70 per cent. is present a still darker picture is produced.

The second class of bodies which act in the same way on a photographic plate are organic substances, and belong essentially to the groups of bodies known as terpenes. In trying to stop the action of metallic zinc, which I thought at the time might arise from vapour given off by the metal, copal varnish was used, but in place of stopping the action it was found to increase it, and this increase of activity was traced to the turpentine contained in the varnish. In experimenting with liquids it is convenient to use small shallow circular glass vessels such as are made for bacteriological experiments, the plate resting on the top of the vessel, and the amount of liquid in the vessel determining the distance through which the action shall take place. The following slide, produced in this way, shows how dark a picture ordinary turpentine produces. All the terpenes are active

bodies. Dipentene is remarkably so ; in a very short time it gives a black picture, and if the action be continued, the dark picture passes away, and you then have a phenomenon corresponding to what photographers call reversal. The strong smelling bodies known as essential oils, such as oil of bergamot, oil of lavender, oil of peppermint, oil of lemons, etc., are all active bodies, and all are known to contain in varying quantities different terpenes ; therefore ordinary scents are active bodies, and this is shown by the following pictures produced by eau de Cologne, by cinnamon, by coffee, and by tea. Certain wines also act in the same way : Sauterne gives a tolerably dark picture, but brandy only a faint one. Other oils than these essential ones are also active bodies : linseed oil is especially so ; olive oil is active, but not nearly as much so as linseed oil ; and mineral oils, such as paraffin oil, are without action on the photographic plate.

Interesting results are obtained with bodies which contain some of these active substances ; for instance, wood will give its own picture, as is shown by the following slides : the first is a section of a young spruce tree, the next a piece of ordinary deal, and the third of an old piece of mahogany. Again, the next slide you will recognise as the picture of a peacock's feather. There is much interest in these pictures of feathers, as they distinguish the brilliant interference colours from those produced by certain pigments ; the beautiful blue in the eye of the peacock's feather is without action on the photographic plate. Butterflies' wings, at least some of them, will draw, as you see, their own pictures. Linseed oil, which is a constituent of all printing ink, makes it an active body, and it can, like the zinc and other active bodies, act through considerable distances. In the picture before you the ink was at a distance of one inch from the plate, and the next slide shows what a remarkably clear and dark picture ordinary printing can produce. As the composition of printing ink varies so does its activity, and here are pieces of three different newspapers which have acted under the same conditions on the same plate, and you see how different the pictures are in intensity. Printed pictures, of course, act in the same way—here is a likeness of Sir H. Tate taken from "The Year's Art." The pictures and printing in *Punch* always print well ; so does the yellow ticket for the Friday evening lectures at the Royal Institution ; also the rude trade-mark on Wills's tobacco, and it is of interest because the red pigment produces a very clear picture, but the blue printing is without action on the plate.

An interesting and important peculiarity of all these actions is that it is able to pass through certain media ; for instance, through a thin sheet of gelatin. Here are two plates of zinc ; both have been scratched by sand-paper ; one is laid directly on the photographic plate, and the other one has a sheet of gelatin, its colour is of no note, laid between it and the sensitive plate ; the picture in this case is, of course, not so sharp as when no gelatin is present, but it is a good and clear likeness of the scratches.

Celluloid is also a body which allows the action to pass through

it, as is seen in this picture of a piece of perforated zinc, a picture which was produced at ordinary temperatures. Gold-beaters' skin, albumen, collodion, gutta-percha, are also bodies which are transparent to the action of the zinc and the other active bodies. On the other hand, many bodies do not allow the transmission of the action through them; for instance, paraffin does not, and among common substances writing-ink does not, as is easily shown by placing ordinary paper with writing on it between the active body and the photographic plate. The active body may conveniently be either a plate of zinc or a card painted with copal varnish and allowed to dry, or a dish of drying oil. The picture of an ordinarily directed envelope shows this opacity of ink well. It is a property long retained by the ink, as this picture of the direction of a letter, written in 1801, shows; also this letter of Dr. Priestley's, dated 1795; and here is also some very faded writing of 1810, which still gives a very good and clear picture. Even if the writing be on parchment, the action passes through the parchment, but not through the ink, and hence a picture is formed.

With bodies which are porous, such as most papers, for instance, the action passes gradually through the interstices, and impresses the plate with a picture of the general structure of the intervening substance. For instance, the following pictures show the structure and the water-mark of certain old and modern writing-papers. Some modern writing-papers are, however, quite opaque; but usually paper allows the action to take place through it, and combining this fact with the fact of strong activity of the printing-ink, the apparently confused appearance produced on obtaining a picture from paper with printing on both sides is accounted for, as the printing on the side away from the photographic plate, as well as that next to it, prints through the paper, and is, of course, reversed.

I hope I have now given you a clear idea how a picture can be produced on a photographic plate in the dark, and the general character and appearance of such pictures. I now pass on to the important question of how they are produced. Moser suggested fifty years ago that there was "dark light," which gave rise to pictures on polished metallic plates, and lately it was suggested that pictures were produced by vapour given off by the metals themselves; the explanation, however, which I have to offer you is, I think, simpler than either of these views, for I believe that the action on the photographic plate is due to the formation of a well-known chemical compound, hydrogen peroxide, which undergoing decomposition acts upon the plate and is the immediate cause of the pictures formed. The complicated changes which take place on the sensitive plate I have nothing to say about on the present occasion, but I desire to convince you, that this body, hydrogen peroxide, is the direct cause of these pictures produced in the dark. Indirect proof has to be resorted to. Water cannot be entirely excluded, for an absolutely dry photographic plate would probably be perfectly inactive, and as long as water is present

peroxide of hydrogen may be there also. But what are the conditions under which these pictures are formed? Only certain metals are capable of producing them. This list of active metals which I have mentioned to you was determined solely by experiment, and when completed it was not evident what common property bound them together. Now, however, the explanation has come, for these are the very metals which most readily cause, when exposed to air and moisture, the formation of this body peroxide of hydrogen. Schönbein showed as long ago as 1860 that when zinc turnings were shaken up in a bottle with a little water hydrogen peroxide was formed, and the delicate tests which we now know for this body show that all the metals I named to you not only can in the presence of moisture produce it, but that their power of doing so follows the same order as their power of acting on a photographic plate. Again, what happened with regard to the organic bodies which act on the photographic plates? I have already mentioned that in experimenting with the metals it was accidentally observed that copal varnish was an active substance producing a picture like that produced by zinc, and that the action was traced to the turpentine present; again a process very much like groping in the dark had to be carried on in order to determine which were active and which inactive organic bodies, and the result obtained was that the active substances essentially belonged to the class of bodies known to chemists as terpenes. Now a most characteristic property of this class of bodies is that in presence of moisture and air they cause the formation of hydrogen peroxide, so that whether a metal or an organic body be used to produce a picture, it is in both cases a body capable, under the circumstances, of causing the formation of hydrogen peroxide. Passing now to experimental facts, which confirm this view of the action on sensitive plates, I may at once say that every result obtained by a metal or by an organic body can be exactly imitated by using the peroxide itself. It is a body now made in considerable quantity, and sold in solution in water. Even when in a very dilute condition it is extremely active. One part of the peroxide diluted with a million parts of water is capable of giving a picture. It can, of course, be used in the glass dishes like any other liquid, but it is often convenient not to have so much water present; and then it is best to take white blotting paper, wet it in the solution of the peroxide, and let it dry in the air. The paper remains active for about twenty-four hours; or, what is still better, take ordinary plaster of Paris, wet it with the peroxide solution, and let it set "in a mould" so as to get a slab of it. This slab increases in activity for the first day or two after making, and retains its activity for a fortnight or more. Such a slab will give a good and dark picture in three or four seconds.

To show how similar the pictures produced by the peroxide and those by zinc are, pictures of a Japanese paper stencil, which had been paraffined to make it quite opaque, have been made by both processes, and are shown with other instances in which turpentine

was used in the following slides. It is also very easy to obtain good pictures with the peroxide alone of the structure of paper, etc.; see, for instance, this one of a five-pound note and these of lace. Again, the strict similarity between the action of the peroxide and that of the metals and organic bodies is further shown by the fact that its action passes through the same media as their action does; and here are good pictures formed by the action of the peroxide after passing through a sheet of these substances. How this singular transmission can be explained, I have treated of elsewhere, and time does not allow of my discussing the matter to-night.

There are many ways in which the bright, active zinc surface can be modified. Draw your finger across it, press your thumb upon it, and you stop its activity, as is shown by the picture it will give. Lay a printed paper on the zinc, and let the contact continue for three-quarters of an hour, at a temperature of  $55^{\circ}$ , then bring the zinc in contact with a sensitive plate, a picture of the printing is formed, but allow the contact between the zinc and printing to continue for eighteen hours at the same temperature, and the picture then given by the zinc is the reverse of the former one. Where the ink has been is now less active than the rest of the plate. Here are slides which show these positive and negative pictures. Another way of modifying the zinc surface is interesting. You have seen that the ordinary zinc surface which has been exposed to air and moisture is quite inactive, but if a bright piece of zinc be immersed in water for about twelve hours, the surface is acted on; oxide of zinc is formed, showing generally a curious pattern. Now, if the plate be dried, it will be found that this oxide is strongly active, and gives a good picture of the markings on the zinc. The oxide evidently holds, feebly combined or entangled in it, a considerable quantity of the hydrogen peroxide, and it requires long drying or heating to a higher temperature to get rid of it. Also, if a zinc plate be attacked by the hydrogen peroxide, the attacked parts become more active than the bright metal. Thus place a stencil on a piece of bright zinc, and expose the plate to the action of an active plaster of Paris slab, or to active blotting-paper for a short time, then, on removing the stencil, the zinc plate will give a very good picture of the stencil. Any inactive body—for instance, a piece of Bristol board or any ordinary soft paper—can be made active by exposing it above a solution of peroxide, or, more slowly, by exposing it to a bright zinc surface. If, for instance, a copper stencil be laid on a piece of Bristol board, and a slab of active plaster of Paris be placed on the stencil for a short time, the Bristol board will even, after it has been removed from the stencil for some time, give a good picture of the stencil. Drying oil and other organic bodies may be used in the same way to change the paper. A curious case of this occurred in printing a coloured advertisement cut out of a magazine, for there appeared printing in the picture which was not in the original. This printing was ultimately traced to an advertisement on the oppo-

site page, which had been in contact with the one which was used ; thus this ghostly effect was produced.

I believe, then, that it is this active body, hydrogen peroxide, which enables us to produce pictures on a photographic plate in the dark. There are many other curious and interesting effects which it can produce, and which I should like to have shown you, had time permitted.

I would only add that this investigation has been carried on in the Davy Faraday Laboratory of this Institution.

[W. J. R.]

Friday, May 12, 1899.

**HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. F.S.A., President,  
in the Chair.**

**PROFESSOR THOMAS PRESTON, M.A. D.Sc. F.R.S.**

*Magnetic Perturbations of the Spectral Lines.*

THE subject which we are about to consider this evening forms a connecting link between two of the most interesting branches of human knowledge—namely, that which treats of magnetism and that which treats of light. Almost as soon as the properties of magnets became known, mere curiosity alone must have prompted philosophers to ascertain if any relation existed between magnetism and “the other forces of nature,” as they were generally termed. We are consequently led to expect, amongst the records of early experimental investigations, some accounts which treat of the action of magnetism on light.

When we seek for such accounts, however, we find that they are almost wholly absent from the literature of science; and this arises, I believe, from the great difficulty of the investigation and from the circumstance that only negative results were obtained, rather than that no such inquiry suggested itself or was undertaken. Even in quite recent times this inquiry has been prosecuted, but without success, by physicists who have published no account of their experiments. We may take it, therefore, that the inquiry is in itself an old one, although it is only now that it has been carried to a successful issue.

The earliest recorded attempt to solve this problem with which we are acquainted, is that of a celebrated British physicist whose name must for ever shed lustre on the annals of the Royal Institution—I speak of Michael Faraday. In order to understand the nature of the investigation which Faraday took in hand, and which has led up to the discourse of this evening, it is best to consider briefly some elementary facts concerning magnetism and light.

In the first place I shall assume that we know in a general way what the peculiarities of a body are which lead us to say that it is magnetised, or a magnet. These are that, when freely suspended, it sets itself in a definite direction over the earth's surface, as illustrated by the compass needle, and that in the space around it there is “magnetic” force exerted on pieces of iron, and in a smaller degree on other substances. For this reason we say that a magnet is surrounded by a magnetic field of force. The field of force is simply the space surrounding the magnet, and it extends to infinity in all directions from the magnet. Near the magnet the force is strong,



and far away from it the force is almost insensible; and so we say that the field is strong at certain places near the magnet, and that it is weak at places far away from the magnet. The direction of the force at any point is the direction in which the north pole of another magnet would be urged if placed at that point, and the push which this pole experiences may be taken to represent the intensity or strength of the magnetic field at the point in question. This is represented diagrammatically by these drawings [referring to figures suspended before the audience], which show roughly the nature of the field of force surrounding an ordinary bar magnet, a horse-shoe magnet, and the much more powerful form—the electro-magnet. It will be seen that the space outside the iron is filled with a system of curved lines running from the north pole to the south pole of the iron core. Where the lines are closest together there the magnetic force is strongest, and the direction of a line at any point is the direction of the resultant magnetic force at that point—that is, the direction in which a north pole would be urged if placed at that point.

Faraday always pictured the magnetic field as filled with lines of force in this way, and the importance of the conception can scarcely be over-rated, for it leads us to view the magnetic action as being transmitted continuously through the intervention of some medium filling all space, rather than by the unintelligible process of direct action at a distance. This medium is called the ether; but as to what it is that is actually going on in the ether around a magnet, we cannot definitely say. It may be that there is a flow of ether along the lines of magnetic force, so that there is an out-flow at one end of the magnet and an in-flow at the other, or it may be that the ether is spinning round the lines of force in the magnetic field. For our present purpose it is not a matter of very much importance what the exact condition of the ether may be in a magnetic field, for if the ether in a magnetic field is either in some peculiar condition of strain or of motion, and if light consists of an undulatory motion propagated through this same ether, then it may be naturally expected that some action should take place when light is propagated through, or radiated in, a magnetic field of force. This is what Faraday suspected; and in order that we may appreciate the problem with which he had to deal, let us place ourselves in his position and ask ourselves the question: "In what manner can we test experimentally if there is any magnetic action on light?"

In answer to this question, the first thing that occurs to us is to pass a beam of ordinary light through the magnetic field, in some chosen direction, and examine by all the means at our disposal if any action has taken place. When this is done we find that no observable effect is produced. But the scientific investigator does not rest satisfied with one negative result. He varies the conditions of the experiment, and returns to the attack with renewed vigour and hopes. In our first trial we passed a beam of light through the air-filled space around the magnet, and we may vary this experiment

either by removing the air altogether, and so causing the beam to traverse a vacuum, or we may replace the air by some dense transparent substance such as glass or water. Under these new conditions we still fail to detect any influence of the magnetic field on a beam of ordinary light. This negative result might arise from the field of force being too weak to produce an observable effect, or it might be that the effect (if any effect really does exist) may be of such a character that it is impossible to detect it with ordinary light. In common light the vibrations take place indifferently in all directions around the ray, and follow no law or order as to their type. They possess no permanent relation to any direction around the ray, so that if the magnetic action should happen to be a twisting of the vibrations round the ray, it will be impossible to detect this twist in the case of ordinary light.

As a matter of fact it is a twist of this kind that actually happens, and this is probably what Faraday anticipated. In order to detect it, therefore, it is necessary to employ a beam of light in which the vibrations are restricted to a single plane passing through the ray. Such light is said to be plane-polarised, and may be obtained by transmitting common light through a doubly refracting crystal. Faraday found that when a beam of this plane-polarised light is passed through the magnetic field, in the direction of the lines of force, a distinct effect takes place, and that the effect is a twisting of the plane of polarisation of the light vibrations as they pass through the magnetic field—or, to be more precise, as the light passes through the matter occupying the field.

This is the Faraday effect. Its magnitude depends on the strength of the field and upon the nature of the matter, through which the light passes in that field. This latter is an important fact that should not be lost sight of in reasoning upon the nature of this effect. The presence of matter in the field appears to be necessary. The effect is not observed in a vacuum, but becomes greater as the field becomes filled with matter of greater density. It is, therefore, not a direct action of the magnetic field on the light vibrations, but rather an indirect action exerted through the intervention of the matter which occupies the magnetic field.

This action, as we have said, is a rotation of the plane of polarisation of the beam of light, and it arises from the circumstance that, in passing through the magnetic field, vibrations which take place from right to left do not travel forward with the same velocity as those which take place from left to right. There is no change in the periods of the vibrations: it is essentially a change of velocity of propagation that occurs. If we examine the transmitted light with a spectroscope, we find that the wave-lengths are unaltered, but that the amount of rotation of the plane of polarisation is different for waves of different lengths. The law which governs the effect is that the rotation of the plane of polarisation varies inversely as the square of the wave-length of the light employed.

You will have noticed that in the foregoing experiment the source of light was placed quite outside the field of magnetic force, while the beam of light was transmitted through the field for examination. Now we might place the source of light itself in the magnetic field, and then examine if the light emitted by it is in any way affected by the magnetic force. This variation of the experiment suggests itself at once, and was indeed also tried by Faraday—in fact it formed his last experimental research of 1862, but without success. The same experiment has been tried, no doubt, by many other physicists, with the same negative result.

The first recorded success, or at least partial success, was by M. Fizee in 1855. He placed the source of light—a gas flame impregnated with sodium vapour—between the pole-pieces of a powerful electro-magnet. This being done, the light radiated by the flame was passed through the slit of a highly dispersive spectroscope and examined. What M. Fizee observed was that the bright spectral lines became broadened by the action of the magnetic field on the radiating source. His account is, perhaps, somewhat confused, owing to his imperfect apprehension of the true nature of the phenomenon which he observed; but, without doubt, he observed a true magnetic effect on the radiated light—namely, this broadening of the spectral lines. But he did not convince the scientific world that he had made any new discovery, and so the matter fell into neglect until it was revived again in 1897 by the now celebrated work of Dr. P. Zeeman.

The credit which attaches to Dr. Zeeman's work is that he not only, after prolonged effort, succeeded in obtaining this new magnetic effect, but he also convinced the world that the effect was a true one, arising from the action of the magnetic field on the source of light. That Dr. Zeeman was able to do this was due, perhaps, as much to the present advanced state of our theoretical knowledge of this subject as to his own skill and perseverance as an observer; and this is a striking example of the great assistance which well-founded theory affords to experimental investigation. The theory connects the facts already known in reasonable and harmonious sequence, predicts new results, and points out the channels through which they must be sought. Without such scientific theory this general systematic advance would be impossible, and new results would be stumbled on only by accident.

To see how this applies to our case, we revert to the fact determined by Dr. Zeeman—namely, that when the source of light is placed in a strong magnetic field the spectral lines become broadened. [Slide shown here.] As soon as this was announced Professor Lorentz, and subsequently Dr. Larmor, examined the question from the theoretical point of view. They analysed the subject mathematically, and came to the conclusion that each spectral line should be not merely broadened, but should be actually split up into three—that is, each line should become three lines, or, as we shall say in future, a triplet. They also arrived at the further most important

and interesting conclusion, viz. that the constituent lines of this triplet must be each plane-polarised—the central line of the triplet being polarised in one plane, while the side lines are polarised in a perpendicular plane. In fact the vibrations of the light forming the central line are parallel to the lines of magnetic force, while the vibrations in the side lines are perpendicular to the lines of force. This prediction of tripling and polarisation from theoretical considerations may be regarded as the key to the subsequent advance that has been made in the investigation of this region of physics. In order to understand it, let us place ourselves in Dr. Zeeman's position when he found that the spectral lines became broadened by the magnetic field, and let us be informed that this broadening is in all probability a tripling of the lines accompanied by plane-polarisation. The question now is, "How are we to determine if this is the case?"

It is clear that if the broadened line is really a triplet, then the components of this triplet must be so close together that they overlap each other, and so appear to the eye merely as one broad line, as illustrated by the model which is here before you. [Model illustrating the overlapping shown here.] We know that the spectral lines are not infinitely narrow lines, but are really narrow bands of light of finite width, and consequently we are quite prepared to regard the magnetically broadened line as an overlapping triplet; but we cannot remain satisfied until we have proved beyond all doubt that it really is a triplet, and not merely a single broad line. To do this, Dr. Zeeman made use of the second prediction of the theory—namely, that the constituents of the triplet must be plane-polarised. If this is so, then the outer edges of the broadened line must be plane-polarised, and therefore by introducing a Nicol's prism into the path of the light it must be possible to turn the Nicol so that the plane-polarised edges shall be cut off, and the breadth of the line shall be reduced to its normal amount. In fact, in this position of the Nicol the outside lines of the triplet are extinguished, and the central component alone remains. This component is, of course, the same in width as the original line, and consequently when the outer members of the triplet are extinguished all the magnetic broadening of the line is removed. When the Nicol is turned through a right angle the central component of the triplet is extinguished, while the side lines remain; and, if these side lines are sufficiently separated so that they do not overlap, then, when the central line is removed, a narrow dark space will exist between the side components, which represents the space intervening between the outer members of the triplet, as illustrated by this photograph. [Slide shown.]

But even though we may be able to so increase the strength of the magnetic field that when the central component of the triplet is removed by a Nicol the side lines stand apart with a clearly defined interval between them, yet this in itself does not absolutely satisfy us that the broadened line is a triplet. It might be contended that

the broadened line is not really a triplet, but is merely a band of light polarised in one plane along its edges and in the perpendicular plane along its centre, and that increase of the magnetic field might never separate it into distinct constituents, but merely continue to broaden it. This contention, however, might be disposed of by a careful study of the facts, even though we might not be able to produce a magnetic field strong enough to completely separate the constituent lines of the triplet.

But clearly the thing to be arrived at is to so arrange matters—in fact, to so design our electro-magnet and to plan the conditions of our experiment—that the magnetic field acting on the source of light shall be strong enough to completely separate the members of the triplet, if such exist. You will understand that this is no easy thing to do when you remember that it was only after repeated efforts and many failures that even a slight broadening of the spectral lines was obtained. Nevertheless, in spite of the great difficulty which besets this investigation, and which arises from our inability to obtain a magnetic field of unlimited strength, yet, with a properly designed magnet and other properly arranged conditions, it is possible to obtain a magnetic field strong enough to completely separate the constituents of the magnetic triplet, and thus to prove that the prediction of theory is verified by the actual facts. [Slide shown.]

But with a magnetic field of great strength the facts as shown by these slides [photographs shown here] turn out to be more complicated and more interesting than the simple theory led us to expect. For while some of the spectral lines are split up into triplets as indicated by theory, some on the other hand become resolved into sextets, or octets, or other complex types. [Slides shown here.] Thus, when the magnetic field becomes sufficiently intense, we realise to the full all the theoretical predictions and more. The reason of this surplus of realisation over expectation lies in the fact that the theory in its simplest form deals only with the simplest types of motion under the simplest conditions, and the conclusions arrived at are of course of corresponding simplicity. When more complicated types of motion are contemplated, the theory furnishes us with the dynamical explanation of the more complicated types of effect produced by the magnetic field. That tripling pure and simple should occur in the case of every spectral line (as predicted by the simplest form of theory) is not a result which we should expect from a broader consideration of the problem. In fact, if we reflect on the subject, we are forced to the conclusion that deviations from the pure triplet type should be expected, and, as we have seen, such deviations actually do occur. In this respect, therefore, the experimental investigation which yields more than the simple theory expected is not to be taken as in any way discordant with that theory, but, on the contrary, to be in harmony with it.

In order that you may form some idea as to what it is that the theory supposes to be in operation in the production of these pheno-

mena, I have had this elliptic frame constructed [model shown], which I ask you for the present to consider as the orbit described by one of those elements of matter which by their motions set up waves in the ether, and thereby emit what we call light. This white ball, which slides on the elliptic frame, is supposed to represent the element of matter. It is sometimes called an ion, which name is used to imply that the element of matter carries an electric charge inherently associated with it.

Now, under ordinary circumstances this ion revolving in its orbit with very great rapidity will continue to do so peacefully, unless external forces come into play to disturb it. When external forces come into action the orbit ceases in general to be the same as before. The orbit becomes perturbed, and the external forces are termed perturbing forces. But you now ask, What is the character of the forces introduced by the magnetic field when the ion is moving through it? In answering this, we are to remember that the ion is supposed to be an element of matter charged with an electric charge—or, if you like, an electric charge possessing inertia. Now, if a charged body moves through a magnetic field, it is an experimental fact that it experiences a force arising from the action of the magnetic field on the moving electric charge. The direction of this force is at right angles both to the direction of motion of the charged body and to the direction of the magnetic force in the field. The effect of this force in our case is to cause the elliptic orbits of the ions to rotate round the lines of magnetic force; or to cause them to have a precessional motion [illustrated by model] instead of staying fixed in space, just as the perturbing forces of the planets in the solar system cause the earth's orbit to have a precessional motion. The angular velocity of this precessional motion is proportional to the strength of the magnetic field, and depends also, as you would expect, on the electric charge and the inertia associated with the ion.

This precessional motion of the orbit, combined with the motion of the ion around the orbit, gives the whole motion of the ion in space, and the result of this combined movement, of these two superposed frequencies—viz. the frequency of revolution of the ion in its orbit, and the frequency of rotation of the orbit around the lines of force—is that, in the case of the light radiated across the lines of force, each period becomes associated with two new periods, or, in other words, each spectral line becomes a triplet. A partial analogue to this, which may to some extent help you to understand the introduction of the two new periods, occurs in the case of sound, although the two phenomena at basis are quite different. The analogue (or quasi-analogue) is this. When two notes of given pitch, that is of given frequency of vibration, are sounded together, their superposition produces two other notes of frequencies which are respectively the sum and the difference of the frequencies of the two given notes. These are known as the summation and the difference tones of the two given notes. Corresponding to these are the two side lines of the

magnetic triplet. The frequency of the vibration in one of these lines is the sum, and the frequency of the other is the difference, of the two frequencies mentioned before—namely, the frequency of the revolution of the ion around its orbit, and the frequency of the precessional revolution of the orbit round the lines of force. The centre line of the triplet has the frequency of the original vibration, and this frequency disappears completely when the light is viewed along the lines of force—that is, through axial holes pierced in the pole-pieces. In this direction, too, a further peculiarity arises, for not only does the triplet drop its central member and become a doublet, but each member of this doublet is not plane-polarised, as the members of the triplet are. They are each, on the contrary, circularly polarised—that is, the vibration is circular instead of being rectilinear.

This all follows as the expectation of the simple theory which supposes that the ions are free to describe their elliptic orbits undisturbed by any forces other than the magnetic field. But it is only to be expected that other perturbing forces must come into play in the assemblage of ions which build up incandescent matter of the source of light. We know, for example, that the other members of the solar system perturb the earth's motion, so that it deviates from the simple elliptic motion predicted by the simple theory which did not take these perturbing forces into account. Hence, if any such perturbing forces exist, and we should be surprised if they did not exist, the tripling pure and simple of the spectral lines will be departed from, and other types will arise. From the character of these new types we may infer the nature of the perturbations which give rise to them, and hence by the study of these types we obtain a view of what is going on in matter when it is emitting light, which we should not possess if such perturbations did not occur. These deviations from pure tripling are consequently of more importance almost, in regard to our future progress, than the discovery of the tripling itself. To give you some idea of the influence of such perturbations in modifying the triplet form, I may mention that it follows from simple theoretical considerations, that if the perturbing forces cause the orbit to revolve in its own plane, or cause it to change its ellipticity periodically, then each line of the triplet produced by the magnetic field will be doubled, and a sextet will result, and other oscillations of the orbit will give rise to other modifications of the normal triplet type. It is not quite easy to see at once, however, what the perturbing forces are exactly, for we do not know the way in which the ions are associated in matter; but if we regard an ion as a charged element of matter describing an orbit, it will be analogous to a closed circuit, or to a magnetic shell, and will be urged to set in some definite way in the magnetic field. In coming into this position it may oscillate about the position of equilibrium, and thus introduce an oscillation into the precessional motion of the orbit, which may have the effect of doubling or tripling the constituents of the pure precessional triplet.

Now, experimental investigation shows us that all the spectral lines do not become triplets when viewed across the lines of force in a magnetic field, for some lines show as quartets, or sextets, or octets, or in general as complex triplets derived from the normal triplet by replacing each component by a doublet or a triplet. We conclude, therefore, that the ions which give rise to these complex forms are not perfectly free in their motions through the magnetic field, but are constrained in some way by association with each other in groups, or otherwise, while they move in the magnetic field.

And now we come to a very important point in this inquiry. According to the simple theory every spectral line, when viewed across the lines of force, should become a triplet in the magnetic field, and the difference of the vibration frequency between the side lines of the triplet should be the same for all the spectral lines of a given substance. In other words, the precessional frequency should be the same for all the ionic orbits, or the difference of wave-length  $\delta\lambda$  between the lateral components of the magnetic triplet should vary inversely as the square of the wave-length of the spectral line under consideration. Now, when we examine this point by experiment, we find that this simple law is very far from being fulfilled. In fact, a very casual survey of the spectrum of any substance shows that the law does not hold even as a rough approximation; for, while some spectral lines show a considerable resolution in the magnetic field, other lines of nearly the same wave-length, in the same substance, are scarcely affected at all. This deviation is most interesting to those who concern themselves with the ultimate structure of matter, for it shows that the mechanism which produces the spectral lines of any given substance is not of the simplicity postulated in the elementary theory of this magnetic effect.

Our previous knowledge of the line spectra of different substances might indeed have led us to suspect some such deviation as this from the results predicted by the simple theory. For if we view the line spectrum of a given substance we find that some of the lines are sharp while others are nebulous or diffuse, and that some are long while others are short—in fact, the lines exhibit characteristic differences which lead us to suspect that they are not all produced by the motion of a single unconstrained ion. On closer scrutiny they are seen to throw themselves into natural groups. For example, in the case of the monad metals (sodium, potassium, etc.), the spectral lines of each metal form three series of natural pairs, and again, in the case of the diad group (cadmium, zinc, etc.), the spectrum of each shows two series of natural triplets, and so on.

Thus, speaking generally, the lines which form the spectrum of a given substance may be arranged in groups which possess similar characteristics as groups. Calling the lines of these groups  $A_1, B_1, C_1 \dots, A_2, B_2, C_2 \dots, A_3, B_3, C_3 \dots$  we may regard the successive groups as repetitions of the first, so that the  $A$ 's—that is  $A_1, A_2, A_3$ , &c.—are corresponding lines produced probably by the same ion; while the  $B$ 's—namely,  $B_1, B_2, B_3$ , &c.—correspond to one



another and are produced by another ion, and so on. This grouping of the spectral lines has been noticed in the case of several substances, and it has been a subject of earnest inquiry amongst spectroscopists for some time past. All such grouping, however, up to the present, has had to depend on the judgment of the observer as to certain similarities in the general character and arrangement of the lines, and similarities which indeed may or may not have any specific relation to the mechanism by which the lines are produced. In fact, such grouping has been effected by guess-work, or by empirical formulæ, and we need not be surprised if it is found that the groups so far obtained are more or less imperfect.

I introduce this grouping of the spectral lines to your notice in order that we may attack the problem of reducing to order the so far apparently lawless magnetic effect. As I have already mentioned, the lines in the spectrum of any given substance are not all resolved into triplets by the magnetic field, but some are resolved into triplets while others become sextets, etc.; and further, the magnitude of this resolution, that is the interval  $\delta\lambda$  between the lateral components does not appear at first sight to obey any simple law.

According to the prediction of the simple theory the separation  $\delta\lambda$  should be proportional to  $\lambda^2$ , and although this law is not at all obeyed, if we take all the lines of the spectrum as a single group, yet we find that it is obeyed for the different groups if we divide the lines into a series of groups. In other words, the corresponding lines  $A_1, A_2, A_3$ , etc. have the same value for the quantity  $e/m$ ,\* or, as we may say, they are produced by the motion of the same ion. The other corresponding lines,  $B_1, B_2, B_3$ , etc. have another common value for  $e/m$ , and are produced therefore by a different ion, and so on. We are thus led by this magnetic effect to arrange the lines of a given spectrum into natural groups, and from the nature of the effect we are led to suspect that the corresponding lines of these groups are produced by the same ion, and therefore that the atom of any given substance is really a complex consisting of several different ions, each of which gives rise to certain spectral lines, and these ions are associated to form an atom in some peculiar way which stamps the substance with its own peculiar properties.

In order to illustrate the meaning of this, let us consider the spectrum of some such metal as zinc. The bright lines forming the spectrum of this metal arrange themselves to a large extent in sets of three—that is, they group themselves naturally in triplets. Denoting these triplets in ascending order of refrangibility by  $A_1, B_1, C_1, A_2, B_2, C_2$ , etc. we find that the lines  $A_1, A_2$ , etc. show the same magnetic effect in character, and have the same value of  $e/m$ , so that they form a series obeying the theoretical law deduced by Lorentz and

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\* The quantity  $e$  is the electric charge of the ion, and  $m$  is its inertia, and the ratio  $e/m$  determines the precessional frequency, or spin, of the ionic orbit round the lines of magnetic force in a given field.

Larmor. In the same way the lines  $B_1, B_2, B_3$ , etc., form another series which also obeys the theoretical law, and possess a common value for the quantity  $e/m$ , similarly for the lines  $C_1, C_2, C_3$ , etc. The value of  $e/m$  for the A series differs from that possessed by the B series or the C series, and this leads us to infer that the atom of zinc is built up of ions which differ from each other in the value of the quantity  $e/m$ , and that each of these different ions is effective in producing a certain series of lines in the spectrum of the metal. When we examine the spectrum of cadmium, or of magnesium—that is, when we examine the spectra of other metals of the same chemical group—we find that not only are the spectra homologous, not only do the lines group themselves in similar groups, but we find in addition that the corresponding lines of the different spectra are *similarly* affected by the magnetic field. And further, not only is the character of the magnetic effect the same for the corresponding lines of the different metals of the same chemical group, but the actual magnitude of the resolution as measured by the quantity  $e/m$  is the same for the corresponding series of lines in the different spectra. This is illustrated in the following table, and leads us to believe, or at least to

Magnetic effect.	Nonets or complex triplets.	Sextets.	Triplets.
Cadmium .. .. $\lambda =$	5086	4800	4678
Zinc .. .. $\lambda =$	4811	4722	4680
Magnesium .. .. $\lambda =$	5184	5173	5167
Precessional spin (approx.) ..	$e/m = 55$	$e/m = 87$	$e/m = 100$

[This table shows the effect for the three lines which form the first natural triplet in the spectrum of cadmium compared with the corresponding lines in the spectra of zinc and magnesium. It will be seen that the corresponding lines in the different spectra suffer the same magnetic effect both in character and magnitude. Thus the corresponding lines 4800, 4722, 5173 are each resolved into sextets, and the rate at which the ionic orbit is caused to precess is the same for each (denoted by  $e/m = 87$  in the table). Similarly for the other corresponding lines.]

suspect, that the ion which produces the lines  $A_1, A_2, A_3$ , etc., in the spectrum of zinc is the same as that which produces the corresponding series  $A_1, A_2, A_3$ , etc., in cadmium, and the same for the corresponding sets in the other metals of this chemical group. In other words, we are led to suspect that not only is the atom a complex composed of an association of different ions, but that the atoms of those substances which lie in the same chemical group are perhaps built up from the same kind of ions, or at least from ions which possess the same  $e/m$ ,

and that the differences which exist in the materials thus constituted arises more from the manner of association of the ions in the atom than from differences in the fundamental character of the ions which build up the atoms; or it may be, indeed, that all ions are fundamentally the same, and that differences in the value of  $e/m$ , or in the character of the vibrations emitted by them, or in the spectral lines produced by them, may really arise from the manner in which they are associated together in building up the atom.

This may be an unjustified speculation, but there can be no doubt as to the fascination which enquiry of this kind has always exerted, and must continue to exert, over the human mind. It is the speculation of the ignorant as well as of the philosophic and trained scientific mind, and even though it should never be proved to rest on any substantial basis of fact, it will continue to cast its charm over every investigator of nature.

It is ever the desire of the human mind to see all the phenomena of nature bound by one connecting chain, and the forging of this chain can be realised only gradually and after great labour in the laboratories of science. From time to time the hope has been entertained that metals may be transmuted, and that one form may be converted into another; and although this hope has been more generally nurtured by avarice and by ignorance rather than by knowledge, yet it is true that we never have had any sufficient reason for totally abandoning that hope, and even though it may never be realised that in practice we shall be able to convert one substance into another, even though the philosopher's stone be for ever beyond our grasp, yet when the recent developments of science, especially in the region of spectrum analysis, are carefully considered, we have, I think, reasonable hope that the time is fast approaching when intimate relations, if not identities, will be seen to exist between forms of matter which have heretofore been considered as quite distinct. Important spectroscopic information pointing in this same direction has been gleaned through a long series of observations by Sir Norman Lockyer on the spectra of the fixed stars, and on the different spectra yielded by the same substance at different temperatures. These observations lend some support to the idea, so long entertained merely as a speculation, that all the various kinds of matter, all the various so-called chemical elements, may be built up in some way of the same fundamental substance; and it is probable that this protyle theory will, in one form or another, continue to haunt the domains of scientific thought, and remain a useful and important factor in our progress, for all time to come.

Even though it may be that a knowledge of the ultimate constitution of matter must for ever remain a sealed book to our enquiries, yet, framed as we are, we must for ever prosecute the extension of our knowledge in every direction; and in pursuing knowledge it frequently happens that vast acquisitions are made through channels which at first seem most unlikely to lead us any further. It has

frequently happened that small and obscure effects, obtained after much labour and difficulty, have led to results of the highest importance, while very pronounced and striking effects which have forced themselves on the attention of the observer have proved comparatively barren. It was by a determined effort of this kind, founded on a correct appreciation of the importance of small outstanding differences—so small as to be despised or passed over by all other observers—that Lord Rayleigh discovered a new gas in our atmosphere, added argon to our list of elements, and initiated the attack which led to the brilliant capture by Prof. Ramsay of several new terrestrial substances.

Viewed from this standpoint I hope I am to some extent justified in occupying your attention this evening with the consideration of the action of magnetism on light, for although the effect produced is small and not easy to observe, yet it is likely to prove an important instrument of research in the study of matter, and it is not inappropriate that a public account of what has been already achieved should be given in this Institution, in which the enquiry was first begun by Faraday, and in which his spirit still lives.

[T. P.]

TUESDAY, JUNE 6, 1899.

H.R.H. THE PRINCE OF WALES, K.G., Vice-Patron,  
in the Chair.

### COMMEMORATION LECTURE,

By the RIGHT HON. LORD RAYLEIGH, M.A: D.C.L. LL.D. F.R.S.,  
Professor of Natural Philosophy *R.I.*

There were also present the Duke of Northumberland (President) the Duke of Devonshire, Lord Lister (Pres. R.S.) Lord Kelvin, Lord Amherst, Sir John Lubbock, Bart. M.P., Sir John Dorington, Bart. M.P., Sir Frederick Abel, Bart., Sir Edward Frankland, Sir Andrew Noble, Sir Henry Thompson, Bart., Sir William Crookes, Dr. J. H. Gladstone, Professor Silvanus P. Thompson, Sir James Crichton-Browne, Sir Frederick Bramwell, Bart., Dr. Ludwig Mond, and Professor Dewar.

LORD RAYLEIGH said that though his was intended to be a commemorative lecture, the idea of commemorating all the work that had been done at the Royal Institution was hopeless. To do so he would require, not one lecture, but many courses of lectures, even though much of it had been in chemistry, which did not fall within his province. Remembering that on other occasions he had spoken in detail of the achievements of Faraday and Tyndall, he thought on this occasion he would do well to go still further back in the century and speak of Dr. Thomas Young, one of the earliest professors of the Institution. Young occupied a very high place in the estimation of men of science—higher, indeed, now than at the time when he did his work. His “Lectures on Natural Philosophy,” containing the substance of courses delivered in the Institution, was a very remarkable book, which was not known as widely as it ought to be. Its expositions in some branches were unexcelled even now, and it contained several things which, so far as he knew, were not to be found elsewhere. The earlier lectures dealt with elementary mechanics, and the reader would find as sound an exposition of that science as could be imagined. It was to Young that they owed the term *energy*, now in everybody’s mouth. Elastic resilience was better dealt with there than in any other treatise he knew of, for Young discussed the subject with remarkable ingenuity, showing that the phenomena exhibited by two bodies coming into collision were comprehended under it. If the velocity was moderate, all their motion might be taken up in them in the form of potential energy; but if it exceeded a certain limit their

integrity could not be preserved. In the case of a grain of sand projected against a sheet of glass, another element, that of time, had to be considered, for it became a question of the propagation of the wave set up by the impact, and if the region traversed by the wave during collision, and alone available as the seat of potential energy, were too small the glass was bound to break. Young again discussed the problem of a ball supported on a column of air or water, and correctly explained that it preserved its stability and did not fall out of the stream owing to centrifugal force. In the province of sound Young was the originator of many of the most important principles on which the doctrine was now expounded, but it was with optics that his name was most closely associated, for he and Fresnel were the builders of the great structure of the undulatory theory. This was a matter that was tolerably familiar. Lord Rayleigh thought he could best utilise the time at his disposal by mentioning some of the points in which Young's good work had been overlooked. In his time a question of discussion was the change of the focus of the eye for varying distances. One suggested explanation, that accommodation was effected by an alteration in the external convexity of the eye, Young proved to be wrong by drowning his eye in water. This virtually eliminated the convexity, yet the power of accommodation remained; and he therefore concluded it was due to a muscular alteration in the internal lens of the eye. He also described the phenomenon of astigmatism and showed his deep knowledge of optical theory by suggesting that its effects could be counteracted by the use of a slightly sloping lens. In the study of compound colours, or chromatics as it was then termed, Young's views were correct, though not universally accepted even yet. Lord Rayleigh showed a modification of the experiment by which he proved that the combination of green and red gave yellow, and illustrated the fact by a further experiment, not Young's, but following his suggestions, which demonstrated to the audience that when the blue and yellow of the spectrum were cut off by solutions of litmus and bichromate of potash respectively the combination of the remaining red and green was obviously yellow. The lecturer next described Young's way of getting rid of the "false light," that interfered so greatly with the brilliance of the effects when Newton's rings were being obtained by means of two glass plates pressed together, and by analysing the colours from such plates with a prism he exhibited the original of a diagram in Young's book, which indicated the particular rays destroyed by interference. Young was singularly successful in the theory of cohesion and capillarity, in which some of his earliest work was done, and he was the first to deduce an estimate of molecular dimensions from *data* afforded by that theory. The size of the molecule, according to his calculations, was not very different from that admitted at the present day. In the theory of the tides he made great advances, and in explaining the circumstances which determine whether there shall be high or low water under the moon, he gave the general theory of forced vibrations.

His views of heat were very interesting. He had the utmost contempt for the idea widely prevalent in his time that it was a separate entity, and expressed the hope that before long philosophers might return to a true conception of its nature as motion. Lord Rayleigh, in concluding his observations on Young, said that possibly he had left the impression that Young knew everything. In fact, it was seldom that he was wrong; but just to show that he was, after all, human, a passage might be quoted from his book in which he declared there was no immediate connection between magnetism and electricity! Speaking of work which had been done at the Institution by men who held no regular appointment in it, the lecturer noted that Wedgwood, in conjunction with Davy, was the first to produce anything that could be called a photograph, while instantaneous photography, such as was required for rapidly moving objects, was carried out for the first time by Fox Talbot in the laboratory of the Institution. Slides were exhibited illustrative of flying bullets, splashing milk, and breaking soap films, all taken by the electric spark. Towards the close of the lecture Lord Rayleigh showed one famous experiment of Faraday's, the rotation of the plane of polarised light by magnetism, which he observed had acquired a new interest from the recent discoveries of Dr. Zeeman. In illustration of Tyndall's work, he instanced the discovery of sensitive flames and their application to acoustical investigation. The analogue of a remarkable optical experiment, from which it appears that there is a bright spot at the centre of the shadow of a circular disc, was exhibited.

SIR JAMES CRICHTON-BROWNE said,

May it please your Royal Highness,

The Royal Institution having resolved to mark its Centenary by adding to its roll of Honorary Members the names of some of the most eminent representatives of physical and chemical science on the Continent and in America, I beg leave to present to you the gentlemen who have been selected for that distinction and who have honoured us with their presence here to-day.

All of them have done worthy and memorable work in the field of science, all of them are of world-wide reputation, and it is unnecessary therefore in an audience like this, and it might be tedious and embarrassing to them that I should recount the offices, achievements, publications and honours of each, and so I shall only present them nominally in asking your Royal Highness to admit them to the Honorary Membership.

The diplomas which have been prepared for them they will carry back with them to almost every country in Europe and to the United States of America—whence came the founder of the Royal Institution to these shores just one hundred and twenty-three years ago—and we feel sure that these diplomas will have an enhanced interest and value for all of them because they are bestowed by the hand of your Royal Highness.

Our conference here this afternoon accentuates the universal brotherhood of science, and so may perhaps do something to promote the concord of the nations.

I have the honour to present the following gentlemen :—Dr. Émile Ador (Geneva), Professor Joseph S. Ames (Baltimore), Professor Svante Arrhenius (Stockholm), Professor George F. Barker (Philadelphia), Professor Carl Barus (Providence, U.S.A.), Professor Henri Becquerel (Paris), Dr. L. Bleekrode (The Hague), Professor Giacomo Luigi Ciamician (Bologna), Professor Nicolas Egorof (St. Petersburg), Professor Antoine Paul Nicolas Franchimont (Leiden), Professor Heinrich Gustav Kayser (Bonn), Professor Wilhelm Korner (Milan), Mr. Samuel Pierpont Langley (Washington), Professor Oscar Liebreich (Berlin), Professor Gustave Leonard Van der Mensbrugge (Ghent), Professor Albert A. Micholson (Chicago), Professor Henri Moissan (Paris), Professor Raffaelo Nasini (Padua), Professor Walther Nernst (Göttingen), and Mr. Ernest Solvay (Brussels). The diploma of honorary membership will be forwarded to the following, who are unable to be present :—Professor Armand Émile Gautier (Paris), Professor Wilhelm Ostwald (Leipzig), Professor Robert H. Thurston (Ithaca), Professor Emilio Villari (Naples), Professor Jules Louis Violle (Paris), and Dr. William L. Wilson (Washington).

As it was thought essential that the Centenary of the Royal Institution should be celebrated in this place, its old, its first, and only home, it was found impossible from want of room to invite delegates from universities, colleges, societies and academies, as the managers would otherwise have wished to do; but notwithstanding that no invitations have been issued, two foreign learned societies have spontaneously sent addresses of congratulation. The German Chemical Society, and the German Society of Chemical Industry, felicitate the Royal Institution on the completion of one hundred years of its existence, generously acknowledge the splendid work it has accomplished without Governmental aid, and simply by private enterprise and individual effort, and hope for it a continuance of that beneficent activity which has never flagged from the days of Rumford down to those of Rayleigh and Dewar.

The addresses are most gratefully received and will be published in the Proceedings of the Institution.

The DUKE OF NORTHUMBERLAND moved a vote of thanks to the Prince of Wales for presiding.

The DUKE OF DEVONSHIRE, in seconding the motion, said that the Royal Institution had contributed in no small degree to the extraordinary advance of science that the century had witnessed. It was entirely in accordance with the principles that guided his Royal Highness in public life that he should have taken a prominent part in the celebration of the Institution which had become a national one. It was obvious that such an Institution as that could not perform all the work of which it was capable unless it met with a large



share of public support, and no small element in obtaining that support was the countenance of his Royal Highness.

The PRINCE OF WALES said: I am deeply sensible of the kind words which have fallen from the lips of the Duke of Northumberland and the Duke of Devonshire. I need hardly assure them, nor any of you ladies and gentlemen present, that I shall always look back with the deepest pleasure and gratification on the fact that I have taken part in the Centenary of the Royal Institution. Having been acquainted with it from my earliest years, and having had the advantage of listening to many of the great scientific men who have given their lectures and shown their experiments in this room, I am glad to think that I have been present on this occasion to hear the interesting, able and exhaustive lecture which Lord Rayleigh has so kindly given us with his excellent experiments. He has been able to go over much ground in a very limited space of time. The interest that I take in this Institution, I assure you, will never be diminished. It has, as the Duke of Devonshire has said, become a national one. It is self-supporting, and during these hundred years has, no doubt, acquired an amount of scientific knowledge which has been appreciated not only by this country but by every part of the world. Amongst the most pleasant of my duties here to-day I count my having been asked to personally deliver the diplomas to the many distinguished gentlemen who come across the water to join with us in this Centenary Festival. As a Member and a Vice-Patron of the Institution, I beg to acknowledge our gratitude to them for having so kindly given us their cordial greetings and presence on this interesting occasion. I regret that I have not time for more. Let me again express my sincere thanks to you. I leave here with feelings of the deepest gratification at having been present on this occasion.

WEDNESDAY, JUNE 7, 1899.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G., President,  
in the Chair.

COMMEMORATION LECTURE,

By PROFESSOR DEWAR, M.A. LL.D. F.R.S. *M.R.I.*,  
Fullerian Professor of Chemistry *R.I.*

There were also present, the Honorary Members, together with Lord Kelvin, Lord Amherst, Sir George Stokes, Sir Andrew Noble, Dr. Ludwig Mond, Sir James Crichton-Browne, Sir Frederick Bramwell, Bart., Sir Frederick Abel, Bart., Sir William Crookes, and Lord Rayleigh.

PROFESSOR DEWAR said:—

My colleague, Lord Rayleigh, in his Commemoration Lecture, dealt so admirably and exhaustively with some of the discoveries of our great predecessors in this Institution, that it will be unnecessary to pursue further the lines of historical treatment in this lecture. Instead of discoursing generally on the chemical side of the work of Davy and Faraday and their successors, it has seemed to me more appropriate to attempt some experimental demonstrations of the latest modern developments in a field of inquiry opened out to science by the labours of the two illustrious chemists just mentioned. With this object in view, my discourse this evening will be confined to the subject of liquid hydrogen. Davy said: "Nothing tends so much to the advancement of knowledge as the application of a new instrument. The native intellectual powers of man in different times are not so much the causes of the different success of their labours as the peculiar nature of the means and artificial resources in their possession." The new instrument of research, which, for the first time we have to experiment with before an audience, is the liquid form of the old inflammable air of Cavendish. Lavoisier towards the end of the last century had the scientific acumen to declare that in his opinion, "if the earth were suddenly transported into a very cold region, the air, or at least some of the æriform fluids which now compose the mass of our atmosphere, would doubtless lose their elasticity for want of a sufficient temperature to retain them in that state. They would return to the liquid state of existence and new liquids would be formed, of whose properties we cannot at present form the most distant idea." Black, about the same time, in discussing the properties of hydrogen, makes the following suggestive observations: "We may now further remark with regard to inflammable air, that it is at present considered as one of the simple or elementary bodies in nature. I mean, however, the basis of it, called the Hydrogen by the French chemists; for the inflammable air itself, namely, hydrogen gas, is considered as a compound of that basis

and the matter of heat. What appearance and properties that basis would have, were it deprived of its latent heat and elastic form, and quite separated from all other matter, we cannot tell." The accuracy of the prophecy of Lavoisier has been experimentally verified, but until recently we had no distinctive answer to the riddle of Black. The object of this lecture will be an attempt to advance the solution of the problem suggested by Black a century ago. It is interesting to note how confident Faraday was that hydrogen would ultimately be obtained in the liquid and solid form. In the course of one of his lectures delivered in the year 1852, he said: "There is reason to believe we should derive much information as to the intimate nature of these non-metallic elements if we could succeed in obtaining hydrogen and nitrogen in the liquid or solid form. Many gases have been liquefied; one carbonic acid gas has been solidified; but hydrogen and nitrogen have resisted all our efforts of this kind. Hydrogen, in many of its relations, acts as though it were a metal; could it be obtained in a liquid or solid condition, the doubt might be settled. This great problem, however, has yet to be solved; nor should we look with hopelessness on this solution; when we reflect with wonder—and, as I do, almost with fear and trembling, on the powers of investigating the hidden qualities of these elements—of questioning them, making them disclose their secrets and tell their tales—given by the Almighty to man." It must be confessed, however, that later physicists and chemists were almost forced to conclude that the problem was a hopeless one. The full history of the liquefaction of hydrogen has been dealt with in a Friday Evening Discourse delivered in January of this year, so that all questions dealing with the work of other investigators may for the present be omitted in order to save time for the experimental illustrations.

This large spherical double-walled and silvered vacuum vessel contains one litre of liquid hydrogen. You observe it is lifted out of a large cylindrical vessel full of liquid air. In order to diminish the rate of evaporation it is necessary to surround the vessel in which the hydrogen is collected with liquid air. Under such conditions the rapidity of evaporation is about the same as that of liquid air when kept in a similar vessel in the ordinary way. In order to prove that hydrogen is present in the liquid form, the simplest experiment is to remove the cotton-wool plug which takes the place of a cork, and insert a metallic wire, to the end of which is attached a ball of asbestos for the purpose of absorbing the liquid. On bringing it quickly into the air and applying a light, it burns with the characteristic appearance of the hydrogen flame (Figure C, Plate III.). The liquid can readily be poured from one variety of vacuum vessel into another, so that by means of this unsilvered cylindrical form the appearance of the liquid and other experiments may be projected on a screen (Figure A, Plate III.) The liquid hydrogen appears in gentle ebullition and is perfectly clear, only there is a white solid deposit in the bottom of the tube, which is really solid air. This may be shown

by removing for an instant the cotton-wool stopper, when you see a snow of solid air falling in the liquid. It is easy to arrange a method of carrying liquid hydrogen in a small vacuum vessel in such a way as to prevent the access of air. This is shown in Plate I., where the vacuum vessel, after it has been filled by dipping it into the main supply by means of a supporting wire, is surrounded with a glass envelope, which becomes filled with an atmosphere of hydrogen gas constantly maintained, thereby preventing the access of air. That the density of the liquid is very small and is altogether unlike liquid air is shown by dropping small pieces of cork, which float readily in the latter liquid, but sink instantly in the hydrogen (Figure B, Plate III.). The real density of the liquid is only one-fourteenth that of water, so that it is by far the lightest known liquid. This small density explains the rapidity with which the liquid is cleared on the entrance of the air snow. The relative smallness of the gas bubbles produced in the actively-boiling liquid which causes an appearance of opalescence, is really due to the small surface tension of the liquid hydrogen. The coefficient of expansion of liquid hydrogen is some five times greater than that of liquid oxygen, and is comparable with that of carbonic acid, about  $5^{\circ}$  from its critical point. The latent heat of evaporation is about 190 units, and the specific heat of the liquid is very high, and so far as my experiments go, leads me to the value 6. This is in very marked contrast to the specific heat of liquid oxygen, which is about 0.5. The extraordinary lowness of its boiling point is at once apparent by cooling a piece of metal in the liquid and then removing it into the air, when it will be seen to condense for a moment solid air on its surface which soon melts and falls as a liquid air. This may be collected in a small cup, and the production of oxygen demonstrated by the ignition of a red-hot splinter of wood after the chief portion of the nitrogen has evaporated. If a long piece of quill tubing sealed at one end, but open at the other, is placed in the liquid, then the part that is cooled rapidly fills with liquid air. On stopping any further entrance of air by closing the end of the tube, the liquid air quickly becomes solid, showing in the interior a hollow spindle from contraction, in passing from the liquid into the solid form (Figure E, Plate III.). On bringing the tube containing the solid from the liquid hydrogen bath into the air we observe liquid air running from the surface while the solid air inside is seen to melt (Figure D, Plate III.). Here is a tube into which liquid oxygen has been poured. On placing it in liquid hydrogen it freezes to a clear blue ice. Liquid nitrogen under similar circumstances forms a colourless ice. If instead of an open tube in free air we employ a closed vessel of about a litre capacity to which the quill tube is attached, then, on repeating the experiment, the same results follow, only the volume of the liquid air formed agrees with the total quantity present in the vessel. This suggests that any air left in the closed vessel must have a very small pressure. This is confirmed by attaching a mercurial gauge to

any vessel containing air, when it will be seen the vacuum produced by hydrogen cooling is equal to that of a Torricellian vacuum (Plate II.). To reach such a high exhaustion the solid oxygen and nitrogen, at the boiling point of hydrogen must be practically non-volatile or have an exceedingly small vapour pressure. If the ordinary air contains free hydrogen, helium, &c. which are non-condensable in this way of working, then the vacuum would not be so high as with pure oxygen or nitrogen. This method may be used to separate the incondensable gases from the air. Such air vacua when examined spectroscopically show the lines of hydrogen, helium and neon. We may now employ this process to produce high vacua, and test their exhaustion by the character of the electric discharge. Vacuum tubes which have been prepared in this way show extraordinary resistance to the passage of the electric discharge; they also show the marked phosphorescence of the glass, characteristic of Crookes tubes (Figures F and G, Plate III.). It is, however, the rapidity with which such high exhaustions can be attained that is so interesting. You will observe that this large Geissler tube, previously exhausted to some three inches pressure, will, when the end part is immersed in liquid hydrogen, pass through all the well-known changes in the phases of striation: the glow on the poles; the phosphorescence of the glass; in the space of a fraction of a minute. From this it follows that theoretically we need not exhaust the air out of our double-walled vessel when liquid hydrogen has to be stored or collected. This makes a striking contrast to the behaviour of liquid air under similar circumstances. The rapid exhaustion caused by the solidification of the air on the surface of a double-walled unexhausted test-tube, when liquid hydrogen is placed in it, may be shown in another way. Leave a little mercury in the vessel containing air, just as if it had been left from making a mercurial vacuum. Now we know mercury, in such a vacuum, can easily be made to distil at the ordinary temperature when we cool a part of the vessel with liquid air, so that we should expect the mercury in the unexhausted test-tube to distil on to the surface cooled with the liquid hydrogen. This actually takes place. A rough comparison of the relative temperatures of boiling hydrogen and oxygen may be made by placing two, nearly identical, hydrogen gas thermometers operating at constant pressure side by side and cooling each with one of the liquids (Plate IV.). It will be seen that the contraction in the thermometer cooled with liquid hydrogen elevates the liquid some six times higher than that of the corresponding liquid column of the thermometer placed in the liquid oxygen. A constant volume hydrogen thermometer constructed as shown in Plate V. gave the boiling point of  $21^{\circ}$  absolute or  $-252^{\circ}$  C., and a similar helium thermometer gave the same result. The critical temperature is about  $32^{\circ}$  absolute or  $-241^{\circ}$  C., and the critical pressure about 15 atmospheres. If a closed vessel is full of hydrogen gas at atmospheric pressure, then, unlike the air vessels, it shows no condensation when a part of it is cooled in liquid hydrogen. To produce

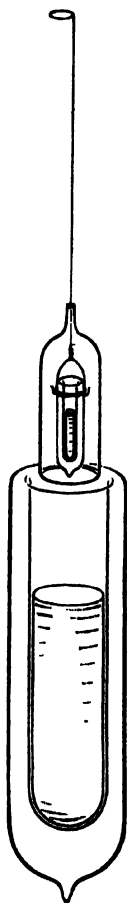
liquefaction we must increase the pressure of the gas, or reduce the boiling point of the liquid hydrogen by exhaustion. Pure hydrogen liquefied in a closed vessel is perfectly clear, showing no trace of colour or any appearance of absorption bands in the position of the spectrum lines. Electric sparks passing in the liquid when examined with the spectroscope show the ordinary line spectrum without any reversals. The vapour of boiling hydrogen is about fifteen times denser than that of the ordinary gas, thus bringing it up to the density of air. The liquid hydrogen, at its boiling point, is about sixty times denser than the vapour coming off. In the case of oxygen the density of the liquid is 255 times that of the vapour at its boiling point.

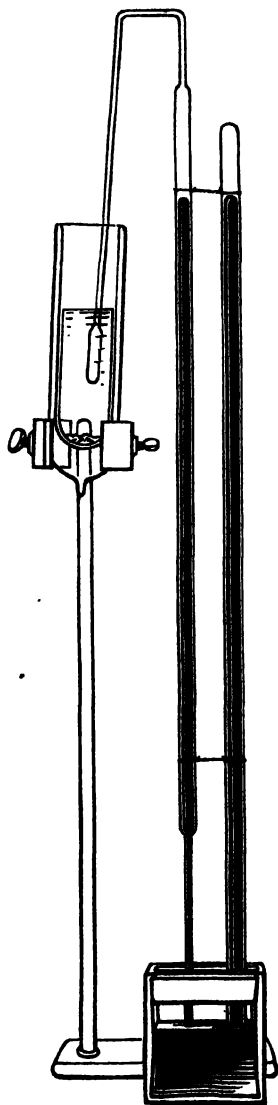
If a piece of cotton wool in the form of a little ball is attached to a thread, placed in liquid hydrogen, and then brought into the magnetic field, it is found to be strongly magnetic. This is simply due to the condensation of solid and liquid air in the pores of the wool. This substance we know is magnetic on account of the oxygen it contains. Pure liquid hydrogen is not magnetic, but when the solid air snow is in suspension in the fluid, then the magnetic character of the latter becomes apparent when the vessel is placed in the magnetic field.

All the phosphorescent effects produced at low temperatures formerly described are intensified at the much lower temperature of boiling hydrogen. To stimulate phosphorescence at the temperature of liquid air, ultra-violet light had to be employed, and then the solid body, organic or inorganic, allowed to rise in temperature. It was during the rise of temperature that the marked luminous emission took place. Amongst inorganic bodies the platino-cyanide of ammonia is very remarkable in this respect, and generally the group in organic chemistry known as the ketonic bodies. In the case of bodies cooled in liquid hydrogen, it appears that some show phosphorescence by simple stimulation with the light coming from an ordinary carbon filament electric lamp. The light in this case coming through glass contains only, we may say, the visible spectra, so that the ultra-violet rays are not now essential. It is strange to find photographic action still relatively considerable. At the boiling point of liquid air the photographic intensity is reduced by 80 per cent. of the value at the ordinary temperature. The photographic effect on a sensitive film immersed in liquid hydrogen as compared with the same placed in liquid air is as one to two, so that 10 per cent. of the action at ordinary temperatures still remains. As every kind of chemical action so far examined is non-existent at this extreme temperature, these experiments suggest that the cause of the photographic action may be essentially physical. No better illustration could be given of the rapid diminution of chemical action at low temperatures than to remind you that fluorine gas, the most active elementary body, under such conditions, may be liquefied and kept in glass vessels.

The effect of a temperature of  $21^{\circ}$  absolute on the electric re-

PLATE I.







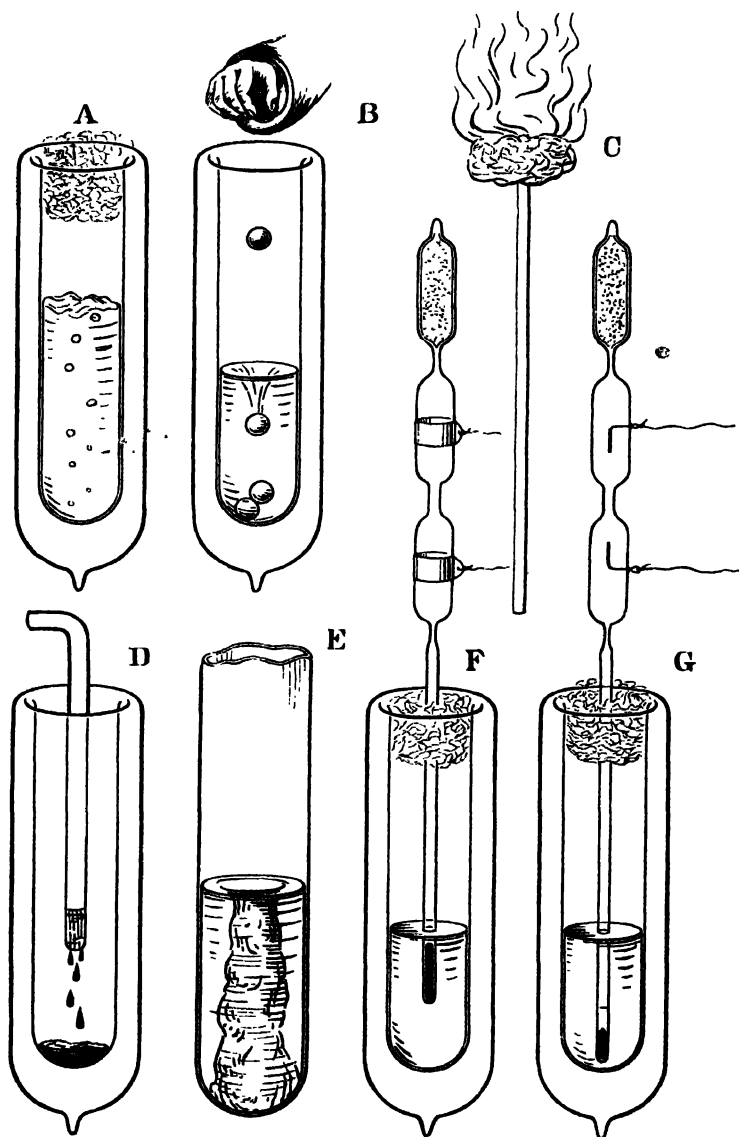
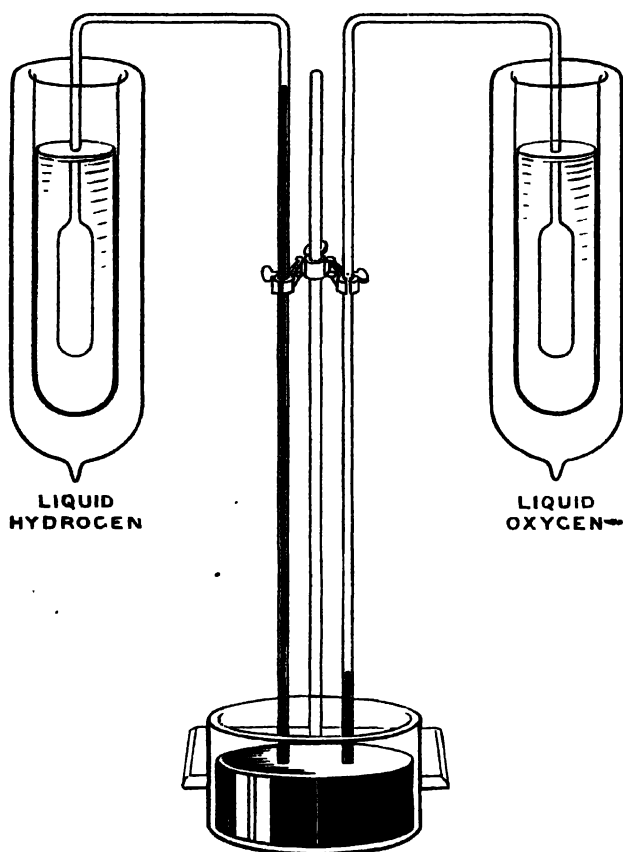
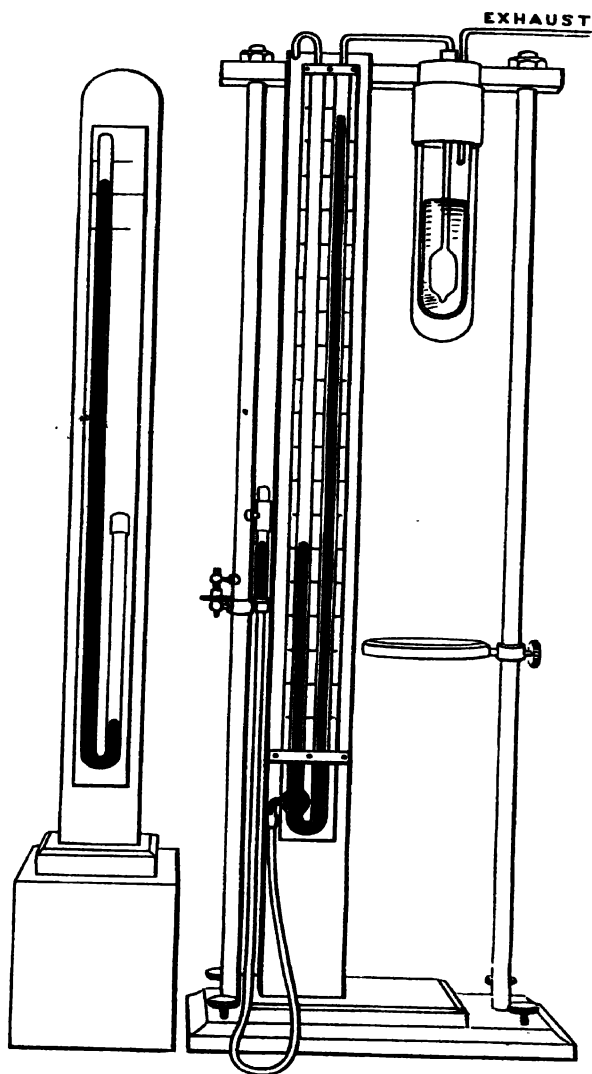


PLATE IV.





sistance of the pure metals is a problem of great interest. In passing from the melting point of ice to the boiling point of hydrogen, pure platinum loses resistance till only  $\frac{1}{40}$  remains, and in the case of electrolytic copper the remaining resistance is only  $\frac{1}{27}$  of what it was at starting. Such results suggest the approach to the condition, of what may be called relatively perfect electric conductivity as the zero of absolute temperature is approached.

Liquid hydrogen is a non-conductor of electricity, and as regards being an insulator for currents of high potential, it is comparable to that of liquid air. The properties of the liquid we have witnessed in no way suggest the metallic character that chemists like Faraday, Dumas and Graham anticipated; and, for the future, hydrogen must be classed with the non-metallic elements.

The liquefaction of hydrogen has been the consequence of some ten years' devotion to low temperature research. To many it may seem that the results have been indeed costly in more ways than one. The scientific worker who prepares the way for future development in this sort of inquiry generally selects complicated methods, and is attracted or diverted into many by-paths of investigation. He may leave to his successors any credit that may be attached to cheapness and ease of production of the agent of research—results that must invariably follow. Liquid hydrogen is an agent of research which will enable us to examine into the properties of matter at the lowest-maintained temperature ever reached by man. Much work has still to be accomplished. One of the most fascinating problems of the study of low temperatures has been materially advanced. The interval separating us from the zero of absolute temperature has been reduced to practically one-fourth the value that it stood at when liquid air was the cooling agent. We can produce in pure Helium instantaneous temperatures bringing us still nearer the goal. Now we can maintain a temperature within less than  $16^{\circ}$  of this zero, and the investigator who will make the further attempt to reduce this distance by an equivalent amount, thereby reaching a steady temperature of  $4^{\circ}$  or  $5^{\circ}$  absolute, will indeed face a problem of almost insuperable difficulty. Well, let us take comfort in an aphorism of Davy's: "Fortunately for the active and progressive nature of the human mind, even experimental research is only a method of approximation to truth."

The success of the demonstration has been largely due to the unremitting exertions of my chief assistant, Mr. Robert Lennox, and to the valuable aid given by Mr. J. W. Heath.

LORD KELVIN, in moving a vote of thanks to Professor Dewar for his brilliant, beautiful, and splendidly interesting lecture, said that if those present wished to measure the importance of the occasion, let them think what Count Rumford, or Davy, or Faraday would have thought, could they have been present. They could not have hoped for their scientific dreams and prophecies to be so splendidly verified

within the century. The end of experiment in research at low temperatures had by no means been reached, and perhaps in a few years substances yet unknown and more refractory than hydrogen would have been found which would bring the experimenter to within five degrees of the absolute zero.

The vote was seconded by SIR GEORGE STOKES and carried by acclamation.

PROFESSOR DEWAR, in reply, referred in appreciative terms to the part taken in the liquefaction of hydrogen by his assistant, Mr. LENNOX. For himself, his chief function had been to get the wherewithal to carry on the experiments, and without the assistance he had received from numerous friends they would have been absolutely impossible.

Diplomas of honorary membership were next presented to Professor CORNU and Professor NEWCOMB.

SIR FREDERICK BRAMWELL proposed a vote of thanks to the Duke of Northumberland for the manner in which he had performed his duties as President of the Institution. C

This was seconded by Dr. MOND and supported by PROFESSOR BARKER, on behalf of the guests from beyond the sea, who, he said, had been royally entertained, listening to lectures such as the world had never before heard, and witnessing experiments such as it had never seen.

The proceedings ended with the reply of the DUKE OF NORTH-UMBERLAND.

Friday, January 19, 1900.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G., President,  
in the Chair.

The RT. HON. LORD RAYLEIGH, M.A. D.C.L. LL.D. F.R.S. M.B.I.  
PROFESSOR OF NATURAL PHILOSOPHY E.I.

*Flight.*

LORD RAYLEIGH first considered the question what people generally meant when they spoke of a flying machine, and concluded that size had a great deal to do with their conception, which was usually of a machine big enough to carry a man by whom it could be controlled: otherwise the flying machine had been invented long since by Penaud. The main problem of the flying machine was the problem of the aeroplane. What were the forces that acted on a plane exposed to the wind? This was also the vital problem of kites, of which he mentioned some of the practical applications by Franklin, Archibald, Baden-Powell, and others; but kites were always anchored to the ground, and as soon as we cast ourselves adrift from the ground the problem became essentially different, for it was then necessary to consider how maintenance in the air could be managed. Now some birds seemed to maintain themselves in the air with little effort. What was the nature of the "soaring" or "sailing flight" by which a big bird maintained himself with but little flapping of the wings? There had been much discussion about this point, often foolish because of misunderstandings between the disputants. However, the science of mechanics enabled it to be laid down with certainty that a bird could no more maintain himself without motion of the wings in a uniform wind moving horizontally than in air at perfect rest. It was entirely a question of relative motion. If, then, a bird was seen to be maintaining himself without flapping, it was certain the air was not moving horizontally and uniformly. But there might be rising currents of air upon which he was supported, and these were much more common than was often supposed. In other cases where it was difficult to imagine the existence of such currents, an explanation might be sought in the non-uniformity of the wind. For example, it was mechanically possible for a bird just at the point of transition between two different *strata* of wind to maintain its position by taking advantage of the different velocities. The albatross, he believed, did something of this sort. Langley, again, had pointed out how the bird could turn to account the internal work of the wind by taking advantage of its gustiness. Leaving this subject, the lecturer discussed the general question of the action of the wind on an aeroplane. He first

showed one or two experiments illustrating the curious effects that might be obtained from a plane exposed obliquely to wind. In one of these it was seen that a light piece of sheet brass, evenly pivoted in, and nearly filling up, an aperture through which air was issuing under pressure, tended to set itself square to the aperture so as to block it as much as possible, but, if started, it continued to rotate in either direction, emitting a roaring sound. This phenomenon had never been properly explained, nor had the somewhat analogous action of a piece of card, which, when dropped, reached the ground with a rotatory motion. As to the pressure of the wind on a horizontal plane surface, if the latter was falling vertically at the rate, say, of four miles an hour, and also moving horizontally at, say, 20 miles an hour, did the horizontal motion make a difference to the pressure that existed at its under surface? It might be argued that it did not; but the argument was fallacious, and the truth was that the horizontal motion much increased the pressure under a vertically falling plane, a fact on which depended the possibility of flight, natural and artificial. Lord Rayleigh showed how this point might be illustrated, and even investigated, by means of a simple variation of the ordinary windmill. This was a light wheel having six vanes, each of which could be set at any desired angle, and it was used by setting four at a particular angle, and finding at what angle the other two must be placed so as to compensate the rotation of the wheel produced by the former when it was moved quickly through the air.\* He next observed that not only was there pressure underneath a bird's wing or an aeroplane, but that the suction above was not an unimportant matter; and he performed an experiment to show the reality of this suction, about which he said there had been some scepticism. Turning to flight on a large scale, he remarked that it was a natural question to ask, Was it possible for a man to raise himself from the ground by working a screw with his own muscular power only? The investigation was not difficult, and the answer was that it was quite impracticable for him to do so. Artificial flight was a question of the speed of the horizontal motion. A bird did not use a revolving mechanism like a screw to propel itself, but he had no doubt that a revolving mechanism was the most suitable for artificial flying-machines. Whether the difficulties of these would be surmounted he did not know, but he was disposed to agree with Mr. Maxim that it was mainly a question of time and much money. Still, he did not think flight would ever be a safe mode of conveyance for those who were desirous of going out for a day's shopping, for it was hard to see how alighting on the ground could ever be rendered quite free from danger. But, as Mr. Maxim once remarked, the first use of flying-machines would be for military purposes, and they had not yet succeeded in making war quite safe.

\* This apparatus was more fully described in the Wilde Lecture (Manchester Memoirs, vol. xliv., Part 4, pp. 1-26), where also some other matters here referred to are treated in greater detail.

Friday, February 23, 1900.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. F.S.A.  
President, in the Chair.

PROFESSOR JOHN H. POYNTING, D.Sc. F.R.S.

*Recent Studies in Gravitation.*

THE studies in gravitation which I am to describe to you this evening will perhaps fall into better order if I rapidly run over the well beaten track which leads to those studies, the track first laid down by Newton, based on astronomical observations, and only made firmer and broader by every later observation.

I may remind you, then, that the motion of the planets round the sun in ellipses, each marking out the area of its orbit at a constant rate, and each having a year proportional to the square root of the cube of its mean distance from the sun, implies that there is a force on each planet exactly proportioned to its mass, directed towards, and inversely as the square of its distance from the sun. The lines of force radiate out from the sun on all sides equally, and always grasp any matter with a force proportional to its mass, whatever planet that matter belongs to.

If we assume that action and reaction are equal and opposite, then each planet acts on the sun with a force proportional to its own mass; and if, further, we suppose that these forces are merely the sum totals of the forces due to every particle of matter in the bodies acting, we are led straight to the law of gravitation, that the force between two masses  $M_1$   $M_2$  is always proportional to the product of the masses divided by the square of the distance  $r$  between them, or is equal to

$$\frac{G \times M_1 \times M_2}{r^2}$$

and the constant multiplier  $G$  is the constant of gravitation.

Since the force is always proportional to the mass acted on, and produces the same change of velocity whatever that mass may be, the change of velocity tells us nothing about the mass in which it takes place, but only about the mass which is pulling. If, however, we compare the accelerations due to different pulling bodies, as for instance that of the sun pulling the earth, with that of the earth pulling the moon, or if we compare changes in motion due to the different planets pulling each other, then we can compare their masses and weigh them, one against another and each against the



sun. But in this weighing our standard weight is not the pound or kilogramme of terrestrial weighings, but the mass of the sun.

For instance, from the fact that a body at the earth's surface, 1000 miles, on the average, from the mass of the earth, falls with a velocity increasing by  $32 \text{ ft. / sec}^2$ , while the earth itself falls towards the sun, 92 million miles away, with a velocity increasing by about  $\frac{1}{2} \text{ inch / sec}^2$ , we can at once show that the mass of the sun is 300,000 times that of the earth. In other words, astronomical observation gives us only the acceleration, the product of  $G \times \text{mass}$  acting, but does not tell us the value of  $G$  nor of the mass acting, in terms of our terrestrial standards.

To weigh the sun, the planets, or the earth, in pounds or kilogrammes, or to find  $G$ , we must descend from the heavenly bodies to earthly matter, and either compare the pull of a weighable mass on some body with the pull of the earth on it, or else choose two weighable masses and find the pull between them.

All this was clearly seen by Newton, and was set forth in his *System of the World* (third edition, page 41).

He saw that a mountain mass might be used, and weighed against the earth by finding how much it deflected the plumb line at its base. The density of the mountain could be found from specimens of the rocks composing it, and the distance of its parts from the plumb line by a survey. The deflection of the vertical would then give the mass of the earth.

Newton also considered the possibility of measuring the attraction between two weighable masses, and calculated how long it would take a sphere a foot in diameter, of the earth's mean density, to draw another equal sphere, with their surfaces separated by  $\frac{1}{4}$ -inch, through that  $\frac{1}{4}$ -inch. But he made a very great mistake in his arithmetic, for while his result gave about 1 month the actual time would only be about  $5\frac{1}{2}$  minutes. Had his value been right, gravitational experiments would have been beyond the power of even Professor Boys. Some doubt has been thrown on Newton's authorship of this mistake, but I confess that there is something not altogether displeasing in the mistake even of a Newton. His faulty arithmetic showed that there was one quality which he shared with the rest of mankind.

Not long after Newton's death the mountain experiment was actually tried, and in two ways. The honour of making these first experiments on gravitation belongs to Bouguer, whose splendid work in thus breaking new ground does not appear to me to have received the credit due to it.

One of his plans consisted in measuring the deflection of the plumb line due to Chimborazo, one of the Andes peaks, by finding the distance of a star on the meridian from the zenith, first at a station on the south side of the mountain where the vertical was deflected, and then at a station to the west, where the mountain attraction was nearly inconsiderable, so that the actual nearly coincided with the geographical vertical. The difference in zenith

distances gave the mountain deflection. It is not surprising that, working in snowstorms at one station, and in sandstorms at the other, Bouguer obtained a very incorrect result. But at least he showed the possibility of such work, and since his time many experiments have been carried out on his lines under more favourable conditions. Now, however, I think it is generally recognised that the difficulty of estimating the mass of a mountain from mere surface chips is insurmountable, and it is admitted that the experiment should be turned the other way about and regarded as an attempt to measure the mass of the mountains from the density of the earth known by other experiments.

These other experiments are on the line indicated by Newton in his calculations of the attraction of two spheres. The first was carried out by Cavendish.

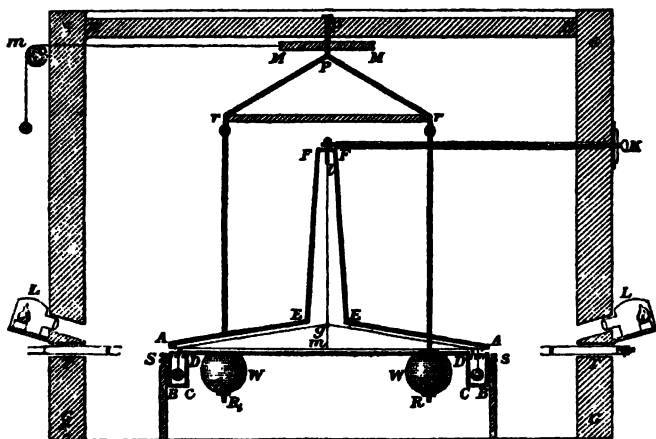


FIG. 1.—Cavendish's Apparatus.

In the apparatus (Fig. 1) he used two lead balls, B B, each 2" in diameter. These were hung at the end of a horizontal rod 6' long, the torsion rod, and this was hung up by a long wire from its middle point. Two large attracting spheres of lead, W W, each 12" in diameter, were brought close to the balls on opposite sides so that their attractions on the balls conspired to twist the torsion rod round the same way, and the angle of twist was measured. The force could be reckoned in terms of this angle by setting the rod vibrating to and fro and finding the time of vibration, and the force came out to less than  $1/3000$  of a grain. Knowing  $M_1$ ,  $M_2$ , and  $r$  the distance between them and the force  $G M_1 M_2 / r^2$ , of course Cavendish's result gives  $G$ , or knowing the attraction of a big sphere on a ball, and knowing the attraction of the earth on the same ball, that is its weight, the

experiment gives the mass of the earth in terms of that of the big sphere, and so its mean density. This experiment has often been repeated, but I do not think it is too much to say that no advance was made in exactness till we come to quite recent work.

By far the most remarkable recent study in gravitation is Professor Boys' beautiful form of the Cavendish experiment, a

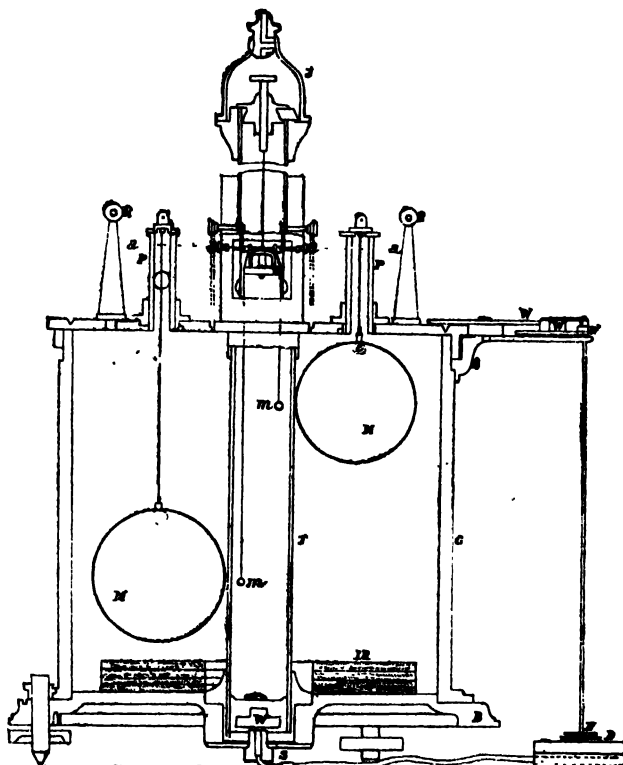


FIG. 2.—Boys' Apparatus.

research which stands out as a model in beauty of design and in exactness of execution (Fig. 2). But as Professor Boys has described his experiment already in this theatre\* it is not necessary for me to more than refer to it. It is enough to say that he made the great discovery, obvious perhaps when made, that the sensitiveness of the apparatus is increased by reducing its dimensions. He therefore

\* Proc. R.I. xiv. part ii. 1894, p. 353.

decreased the scale as far as was consistent with exact measurement of the parts of the apparatus, using a torsion rod, itself a mirror, only 2" long, gold balls, *m m*, only  $\frac{1}{4}$ " in diameter, and attracting lead masses, *M M*, only  $4\frac{1}{4}$ " in diameter. The force to be measured was less than  $1/5 \times 10^6$  grain.

The exactness of his work was increased by using as suspending wire one of his quartz threads. It would be difficult to overestimate the service he has rendered in the measurement of small forces by the discovery of the remarkable properties of these threads.

One of the chief difficulties in the measurement of these small gravitational pulls is the disturbances which are brought about by the air currents, which blow to and fro and up and down inside the apparatus, producing irregular motions in the torsion rod. These, though much reduced, are not reduced in proportion to the diminution of the apparatus.

A very interesting repetition of the Cavendish experiment has lately been concluded by Dr. Braun \* at Mariaschein in Bohemia, in which he has sought to get rid of these disturbing air currents by suspending his torsion rod in a receiver which was nearly exhausted, the pressure being reduced to about  $\frac{1}{200}$  of an atmosphere. The gales which have been the despair of other workers were thus reduced to such gentle breezes that their effect was hardly noticeable. His apparatus was nearly a mean proportional between that of Cavendish and Boys, his torsion rod being about 9" long, the balls weighing 54 gms.—less than two ounces—and the attracting masses either 5 or 9 kgs. His work bears internal evidence of great care and accuracy, and he obtained almost exactly the same result as Professor Boys.

Dr. Braun carried on his work far from the usual laboratory facilities, far from workshops, and he had to make much of his apparatus himself. His patience and persistence command our highest admiration.

I am glad to say that he is now repeating the experiment, using as suspension a quartz fibre supplied to him by Professor Boys in place of the somewhat untrustworthy metal wire which he used in the work already published.

Professor Boys has almost indignantly disclaimed that he was engaged on any such purely local experiment as the determination of the mean density of the earth. He was working for the Universe, seeking the value of *G*, information which would be as useful on Mars or Jupiter or out in the stellar system as here on the earth. But perhaps we may this evening consent to be more parochial in our ideas, and express the results in terms of the mean density of the earth. In such terms then both Boys and Braun find that density 5.527 times the density of water, agreeing therefore to 1 in 5000.

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\* *Denkschriften der Math. Wiss. Classe der Kais. Akad. der Wissenschaften Wien*, lxiiv. 1896.

There is another mode of proceeding which may be regarded as the Cavendish experiment turned from a horizontal into a vertical plane, and in which the torsion balance is replaced by the common balance. This method occurred about the same time to the late Professor U. Jolly and myself. The principle of my own experiment\* will be sufficiently indicated by Fig. 3. A big bullion balance with a 4-foot beam had two lead spheres, A B, each about 50 lbs. in weight, hanging

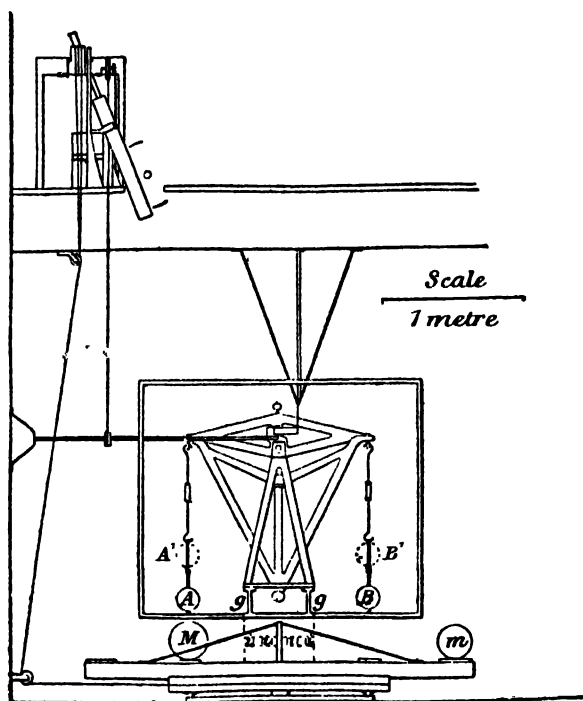


FIG. 3.—Common Balance Experiment (Poynting).

from the two ends in place of the usual scale pans. A large lead sphere, M, 1' in diameter and weighing about 350 lbs., was brought first under one hanging weight, then under the other. The pull of the lead sphere acted first on one side alone and then on the other so that the tilt of the balance beam when the sphere was moved round was due to twice the pull. By means of riders the tilt and therefore the pull was measured directly as so much increase in weight. This increase, when the sphere was brought directly under the hanging

\* Phil. Trans. 182, 1891, A, p. 565.

weight with 1' between the centres, was about  $\frac{1}{2}$  mgm. in a total weight of 20 kgm. or about 1 in 100,000,000. If then a sphere one foot away pulls with  $1/10^8$  of the earth's pull, the earth being on the average 20,000,000 feet away, it is easy to see that the earth's mass is calculable in terms of the mass of the sphere, and its density is at once deduced. The direct aim of this experiment, then, is not G, but the mass of the earth.

It is not a little surprising that the balance could be made to indicate such a small increase in weight as 1 in 100 million. But not only did it indicate, it measured the increase, with variations usually well within 1% of the double attraction, or to 1 in 5000 million of the whole weight, a change in weight which would occur merely if one of the spheres were moved  $\frac{1}{10}$  inch nearer the earth's centre. This accuracy is only attained by never lifting the knife edges and planes during an experiment, thus keeping the beam in the same state of strain throughout, and, further, by taking care that none of the mechanism for moving the weights or riders shall be attached in any way to the balance or its case; two conditions which are absolutely essential if we are to get the best results of which the balance is capable.

Quite recently another common balance experiment has been brought to a conclusion by Professor Richarz and Dr. Krigar-Menzel\* at Spandau, near Berlin. Their method may be gathered from Fig. 4. A balance of 23 cm., say 9-inch beam, was mounted above a huge lead pile about 2 metres cube, and weighing 100,000 kgm.

Two pans were supported from each end of the beam, one pan above, the other pan below the lead cube, the suspending wires of the lower pans going through narrow vertical tubular holes in the lead. Instead of moving the attracting mass, the attracted mass was moved. Masses of 1 kgm. each were put first, say, one in the upper right-hand pan, the other in the lower left-hand pan, when the pull of the lead block made the right hand heavier and the left hand lighter. Then the weights were changed to the lower right hand and the upper left hand, when the pulls of the lead pile were reversed. When we remember that in my experiment a lowering of the hanging sphere by  $1\frac{1}{2}$  inches would give an effect as great as the pull I was measuring, it is evident that here the approach to and removal from the earth by over 2 metres would produce very considerable changes in weight, and, indeed, these changes masked the effect of the attraction of the lead. Preliminary experiments had, therefore, to be made before the lead pile was built up, to find the change in weight due to removal from upper to lower pan, and this change had to be allowed for. The quadruple attraction of the lead pile came out at 1.3664 mgm., and the mean density of the earth at 5.505.

\* Anhang zu den Abhandlungen der Königl. Preuss. Akad. der Wissenschaften zu Berlin, 1898.

This agrees nearly with my own result of 5.49, and it is a curious coincidence that the two most recent balance experiments agree very nearly at, say 5.5, and the two most recent Cavendish experiments agree at, say 5.53. But I confess I think it is merely a coincidence. I have no doubt that the torsion experiment is the more exact, though probably an experiment on different lines was worth making. And I am quite content to accept the value 5.527 as the standard value for the present.

And so the latest research has amply verified Newton's celebrated guess that "the quantity of the whole matter of the Earth may be five or six times greater than if it consisted all of water."

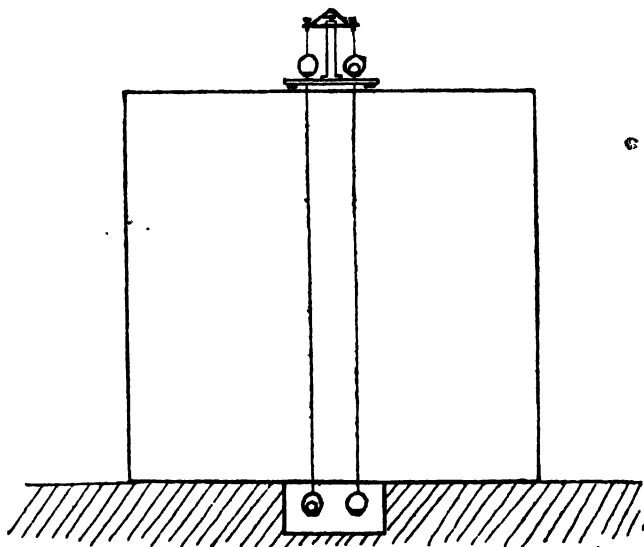


FIG. 4.—Common Balance Experiment (Richarz and Krigar-Menzel).

I now turn to another line of gravitational research. When we compare gravitation with other known forces (and those which have been most closely studied are electric and magnetic forces) we are at once led to inquire whether the lines of gravitative force are always straight lines radiating from or to the mass round which they centre, or whether, like electric and magnetic lines of force, they have a preference for some media and a distaste for others. We know, for example, that if a magnetic sphere of iron or cobalt or manganese is placed in a previously straight field, its permeability is greater than the air it replaces, and the lines of force crowd into it, as in Fig. 5. The magnetic action is then stronger in the presence of the sphere near the ends of a diameter parallel to the original course of the lines

of force, and the lines are deflected. If the sphere be diamagnetic, of water, or copper, or bismuth, the permeability being less than that of air, there is an opposite effect, as in Fig. 6, and the field is weakened at the end of a diameter parallel to the lines of force, and again the lines are deflected. Similarly, a dielectric body placed in an electric field gathers in the lines of force, and makes the field where the lines enter and leave stronger than it was before.

If we enclose a magnet in a hollow box of soft iron placed in a magnetic field, the lines of force are gathered into the iron and largely cleared away from the inside cavity, so that the magnet is screened from external action.

Now, common experience might lead us at once to say that there is no very considerable effect of this kind with gravitation. The evidence of ordinary weighings may, perhaps, be rejected, inasmuch as both sides will be equally affected as the balance is commonly used. But a spring balance should show if there is any large effect when used in different positions above different media, or in different

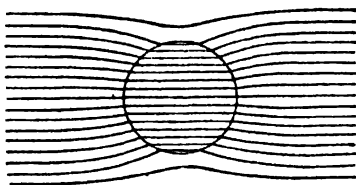


FIG. 5.—Paramagnetic sphere placed in a previously straight field.

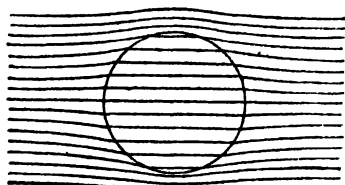


FIG. 6.—Diamagnetic sphere placed in a previously straight field.

enclosures. And the ordinary balance is used in certain experiments in which one weight is suspended beneath the balance case, and surrounded, perhaps, by a metal case, or perhaps, by a water-bath. Yet no appreciable variation of weight on that account has yet been noted. Nor does the direction of the vertical change rapidly from place to place, as it would with varying permeability of the ground below. But perhaps the agreement of pendulum results, whatever the block on which the pendulum is placed, and whatever the case in which it is contained, gives the best evidence that there is no great gathering in, or opening out of the lines of the earth's force by different media.

Still, a direct experiment on the attraction between two masses with different media interposed was well worthy of trial, and such an experiment has lately been carried out in America by Messrs. Austin and Thwing.\* The effect to be looked for will be understood from Fig. 7. If a medium more permeable to gravitation is interposed

\* *Physical Review*, v. 1897, p. 294.



between two bodies, the lines of force will move into it from each side, and the gravitative pull on a body, near the interposed medium on the side away from the attracting body, will be increased.

The apparatus they used was a modified kind of Boys' apparatus (Fig. 8). Two small gold masses in the form of short vertical wires, each .4 gm. in weight, were arranged at different levels at the ends virtually of a torsion rod 8 mm. long. The attracting masses  $M_1$ ,  $M_2$  were lead, each about 1 kgm. These were first in the positions shown by black lines in the figure, and were then moved into the positions shown by dotted lines. The attraction was measured first when merely the air and the case of the instrument intervened, and then when various slabs, each 3 cm. thick, 10 cm. wide and 29 cm. high, were interposed. With screens of lead, zinc, mercury, water, alcohol or glycerine, the change in attraction was at the most about 1 in 500, and this did not exceed the errors of experiment. That is, they found no evidence of a change in pull with change of medium.

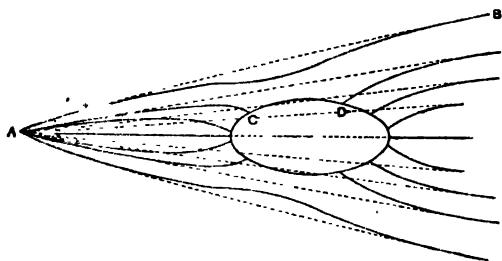


FIG. 7.—Effect of interposition of more permeable medium in radiating field of force.

If such change exists, it is not of the order of the change of electric pull with change of medium, but something far smaller. Perhaps, it still remains just possible, that there are variations of gravitational permeability comparable with the variations of magnetic permeability in media such as water and alcohol.

Yet another kind of effect might be suspected. In most crystal-line substances the physical properties are different along different directions in a crystal. They expand differently, they conduct heat differently, and they transmit light at different speeds in different directions. We might, then, imagine that the lines of gravitative force spread out from, say a crystal sphere unequally in different directions. Some years ago, Dr. Mackenzie\* made an experiment in America in which he sought for direct evidence of such unequal distribution of the lines of force. He used a form of apparatus like that of Professor Boys (Fig. 2), the attracting masses being calc spar spheres about 2 inches in diameter. The attracted masses in one experiment were small lead spheres about  $\frac{1}{2}$  gm. each, and he

measured the attraction between the crystals and the lead when the axes of the crystals were set in various positions. . But the variation in the attraction was merely of the order of error of experiment. In another experiment the attracted masses were small calc spar crystal cylinders weighing a little more than  $\frac{1}{2}$  gm. each. But again there was no evidence of variation in the attraction with variation of axial direction.

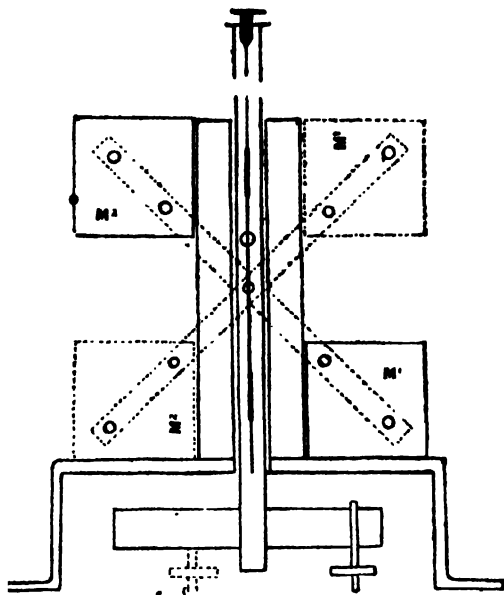


FIG. 8.—Experiment on gravitative permeability (Austin and Thwing).

Practically the same problem was attacked in a different way by Mr. Gray and myself.\* We tried to find whether a quartz crystal sphere had any directive action on another quartz crystal sphere close to it, whether they tended to set with their axes parallel or crossed.

It may easily be seen that this is the same problem by considering what must happen if there is any difference in the attraction between two such spheres when their axes are parallel and when they are crossed. Suppose, for example, that the attraction is always greater when their axes are parallel, and this seems a reasonable supposition, inasmuch as in straightforward crystallisation successive parts of the crystal are added to the existing crystal, all with their axes parallel. Begin, then, with two quartz crystal spheres near each other with their axes in the same plane, but perpendicular to

\* Phil. Trans. 192, 1899, A, p. 245.

each other. Remove one to a very great distance, doing work against their mutual attractions. Then, when it is quite out of range of appreciable action, turn it round till its axis is parallel to that of the fixed crystal. This absorbs no work if done slowly. Then let it return. The force on the return journey at every point is greater than the force on the outgoing journey, and more work will be got out than was put in. When the sphere is in its first position, turn it round till the axes are again at right angles. Then work must be done on turning it through this right angle to supply the difference between the outgoing and incoming works. For if no work were done in the turning, we could go through cycle after cycle, always getting a balance of energy over, and this would, I think, imply either a cooling of the crystals or a diminution in their weight, neither supposition being admissible. We are led, then, to say that if the attraction with parallel axes exceeds that with crossed axes, there must be a directive action resisting the turn from the crossed to the parallel positions. And conversely, a directive action implies axial variation in gravitation. c

The straightforward mode of testing the existence of this directive action would consist in hanging up one sphere by a wire or thread, and turning the other round into various positions, and observing whether the hanging sphere tended to twist out of position. But the action, if it exists, is so minute, and the disturbances due to air currents are so great, that it would be extremely difficult to observe its effect directly. It occurred to us that we might call in the aid of the principle of forced oscillations, by turning one sphere round and round at a constant rate, so that the couple would act first in one direction and then in the other, alternately, and so set the hanging sphere vibrating to and fro. The nearer the complete time of vibration of the applied couple to the natural time of vibration of the hanging sphere, the greater would be the vibration set up. This is well illustrated by moving the point of suspension of a pendulum to and fro in gradually decreasing periods, when the swing gets longer and longer, till the period is that of the pendulum, and then decreases again. Or by the experiment of varying the length of a jar resounding to a given fork, when the sound suddenly swells out as the length becomes that which would naturally give the same note as the fork. Now, in looking for the couple between the crystals, there are two possible cases. The most likely is that in which the couple acts in one way while the turning sphere is moving from parallel to crossed, and in the opposite way during the next quarter turn from crossed to parallel. That is, the couple vanishes four times during the revolution, and this we may term a quadrantal couple. But it is just possible that a quartz crystal has two ends like a magnet, and that like poles tend to like directions. Then the couple will vanish only twice in a revolution, and may be termed a semicircular couple. We looked for both, but it is enough now to consider the possibility of the quadrantal couple only.

Our mode of working will be seen from Fig. 9. The hanging sphere, .9 cm. in diameter and 1 gm. in weight, was placed in a light aluminium wire cage with a mirror on it, and suspended by a long

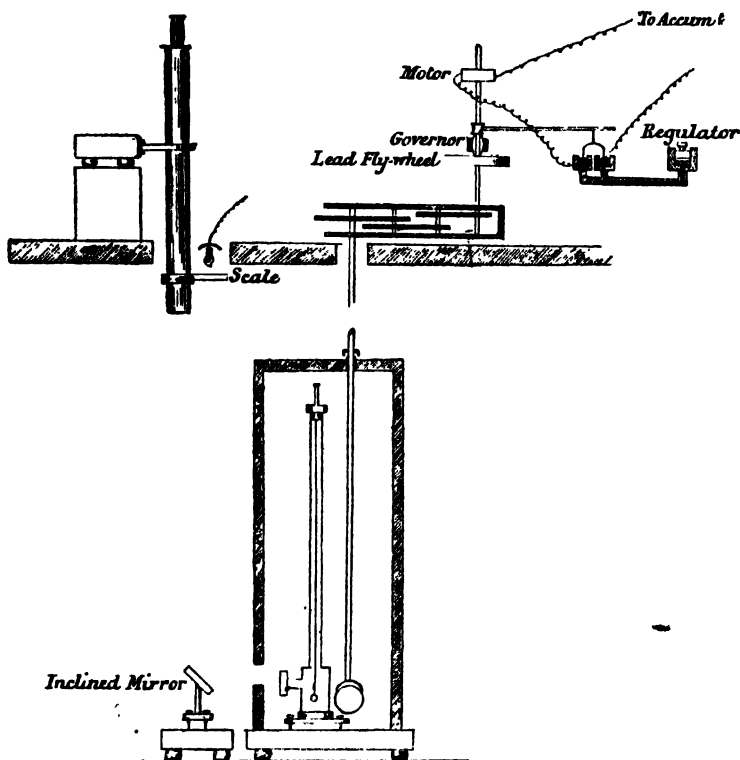


FIG. 9.—Experiment on directive action of one quartz crystal on another.

quartz fibre in a brass case with a window in it opposite the mirror, and surrounded by a double-walled tinfoiled wood case. The position of the sphere was read in the usual way by scale and telescope. The time of swing of this little sphere was 120 seconds.

A larger quartz sphere 6.6 cm. diameter and weighing 400 gms., was fixed at the lower end of an axis which could be turned at any desired rate by a regulated motor. The centres of the spheres were on the same level and 5.9 cm. apart. On the top of the axis was a wheel with 20 equidistant marks on its rim, one passing a fixed point every 11.5 seconds.

It might be expected that the couple, if it existed, would have the greatest effect if its period exactly coincided with the 120 second

period of the hanging sphere—i. e. if the larger sphere revolved in 240 seconds. But in the conditions of the experiment the vibrations of the small sphere were very much damped, and the forced oscillations did not mount up as they would in a freer swing. The disturbances, which were mostly of an impulsive kind, continually set the hanging sphere into large vibration, and these might easily be taken as due to the revolving sphere. In fact, looking for the couple with exactly coincident periods would be something like trying to find if

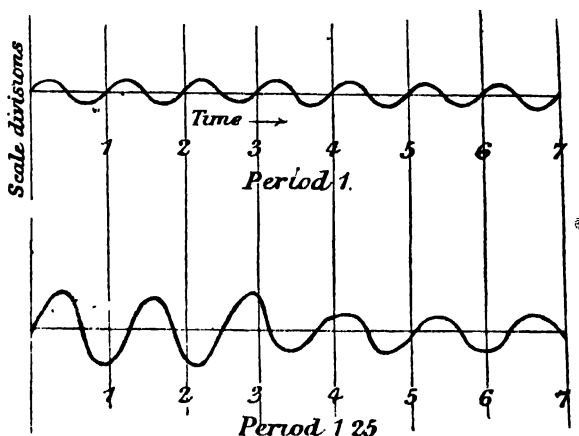


Fig. 10.—Upper curve a regular vibration. Lower curve a disturbance dying away.

a fork set the air in a resonating jar vibrating when a brass band was playing all round it. It was necessary to make the couple period, then, a little different from the natural 120 second period, and, accordingly, we revolved the large sphere once in 230 seconds, when the supposed quadrantal couple would have a period of 115 seconds.

Figs. 10 and 11 may help to show how this enabled us to eliminate the disturbances. Let the ordinates of the curves in Fig. 10 represent vibrations set out to a horizontal time scale. The upper curve is a regular vibration of range  $\pm 3$ , the lower a disturbance beginning with range  $\pm 10$ . The first has period 1, the second period 1.25. Now cutting the curves into lengths equal to the period of the shorter time of vibration, and arranging the lengths one under the other as in Fig. 11, it will be seen that the maxima and the minima of the regular vibration always fall at the same points, so that, taking 7 periods and adding up the ordinates, we get 7 times the range, viz.  $\pm 21$ . But in the disturbance the maxima and minima fall at different points, and even with 7 periods only, the range is from  $+16$  to  $-13$ , or less than the range due to the addition of the much smaller regular vibration.

In our experiment, the couple, if it existed, would very soon establish its vibration, which would always be there and would go through all its values in 115 seconds. An observer, watching the wheel at the top of the revolving axis, gave the time signals every 11.5 seconds, regulating the speed, if necessary, and an observer at the telescope gave the scale reading at every signal, that is, 10 times during the period. The values were arranged in 10 columns, each horizontal line giving the readings of a period. The experiment was carried on for about  $2\frac{1}{2}$  hours at a time, covering, say, 80 periods. On adding up the columns, the maxima and minima of the couple effect would always fall in the same two columns, and so the addition would give 80 times the swing, while the maxima and minima of the

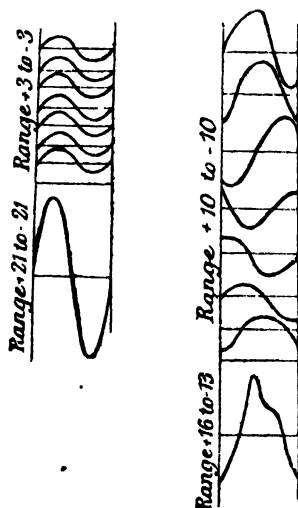


FIG. 11.—Results of superposition of lengths of curves in Fig. 10 equal to the period of the regular one.

natural swings due to disturbances would fall in different columns, and so, in the long run, neutralise each other. The results of different days' work might, of course, be added together.

There always was a small outstanding effect such as would be produced by a quadrantal couple, but its effect was not always in the same columns, and the net result of about 350 period observations was that there was no 115 second vibration of more than 1 second of arc, while the disturbances were sometimes 50 times as great.

The semicircular couple required the turning sphere to revolve in 115 seconds. Here, want of symmetry in the apparatus would come in with the same effect as the couple sought, and the outstanding result was, accordingly, a little larger.

But in neither case could the experiments be taken as showing a real couple. They only showed that, if it existed, it was incapable of producing an effect greater than that observed.

Perhaps the best way to put the result of our work is this: Imagine the small sphere set with its axis at  $45^\circ$  to that of the other. Then the couple is not greater than one which would take  $5\frac{1}{4}$  hours to turn it through that  $45^\circ$  to the parallel position, and it would oscillate about that position in not less than 21 hours.

The semicircular couple is not greater than one which would turn from crossed to parallel position in  $4\frac{1}{2}$  hours, and it would oscillate about that position in not less than 17 hours.

Or, if the gravitation is less in the crossed than in the parallel position, and in a constant ratio, the difference is less than 1 in 16,000 in the one case and less than 1 in 2800 in the other.

We may compare with these numbers the difference of rate of travel of yellow light through a quartz crystal along the axis and perpendicular to it. That difference is of quite another order, being about 1 in 170.

As to other possible qualities of gravitation, I shall only mention that quite indecisive experiments have been made to seek for an alteration of mass on chemical combination,\* and that at present there is no reason to suppose that temperature affects gravitation. Indeed, as to temperature effect, the agreement of weight methods and volume methods of measuring expansion with rise of temperature is good, as far as it goes, in showing that weight is independent of temperature.

So while the experiments to determine  $G$  are converging on the same value, the attempts to show that, under certain conditions, it may not be constant, have resulted so far in failure all along the line. No attack on gravitation has succeeded in showing that it is related to anything but the masses of the attracting and the attracted bodies. It appears to have no relation to physical or chemical condition of the acting masses or to the intervening medium.

Perhaps we have been led astray by false analogies in some of our questions. Some of the qualities we have sought and failed to find, qualities which characterise electric and magnetic forces, may be due to the polarity, the + and -, which we ascribe to poles and charges, and which have no counterpart in mass.

But this unlikeness, this independence of gravitation of any quality but mass, bars the way to any explanation of its nature.

The dependence of electric forces on the medium, one of Faraday's grand discoveries for ever associated with the Royal Institution, was the first step which led on to the electromagnetic theory of light now so splendidly illustrated by Hertz's electromagnetic waves. The quantitative laws of electrolysis, again due

\* Landolt, *Zeit. für Phys. Chem.* xii. 1, 1894. Sanford and Ray, *Physical Review*, v. 1897, p. 247.

to Faraday, are leading, I believe, to the identification of electrification and chemical separation, to the identification of electric with chemical energy.

But gravitation still stands alone. The isolation which Faraday sought to break down is still complete. Yet the work I have been describing is not all failure. We at least know something in knowing what qualities gravitation does not possess, and when the time shall come for explanation all these laborious and, at first sight, useless experiments will take their place in the foundation on which that explanation will be built.

[J. H. P.]



Friday, April 6, 1900.

SIR FREDERICK BRAMWELL, BART., D C.L. LL.D. F.R.S.,  
Honorary Secretary and Vice-President, in the Chair.

PROFESSOR DEWAR, M.A. LL.D. D.Sc. F.R.S. M.R.I.

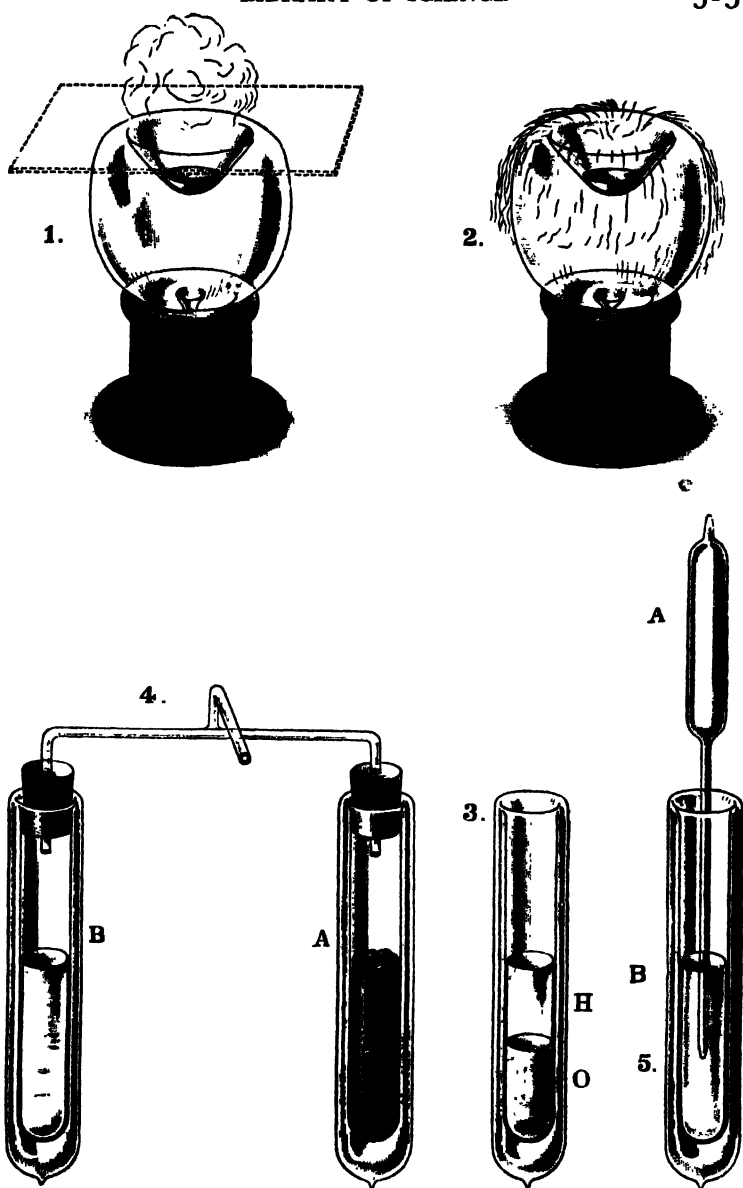
*Solid Hydrogen.*

BEFORE proceeding to discuss the immediate subject of this lecture, it will be advisable to contrast experimentally some of the properties of hydrogen, nitrogen and oxygen in the liquid condition. The two vacuum cups (Figs. 1 and 2) are charged half full respectively with liquid hydrogen and liquid air. When the cup containing the liquid air is placed in front of the electric lamp, the image thrown on the screen reveals the continual overflow of a dense vapour round the outer walls of the vessel. The saturated vapour coming from the steady ebullition of liquid air is three times denser than the free air of the room, and the result is it falls through that air just as if it were a dense gas like carbonic acid or ether vapour. To observe this phenomenon, the vacuum cup must be shallow, otherwise the vapour gets heated up before reaching the mouth of the vessel, and no difference of density in the air coming off is observed. We will now project the image of the cup containing liquid hydrogen, covered loosely in this case with a glass plate, upon the screen; here, no heavy vapour escaping round the sides is visible. The vapour of the boiling liquid hydrogen has a density nearly equal to the air of the room, but as it gets very rapidly heated up by the glass cover the gas that is escaping is seen to rise in air like any light gas. On now removing the glass plate, a very different phenomenon is observed, which contrasts markedly with the behaviour of the liquid air in the former vessel. The cup and the air above is filled with a dense surging snowstorm of solid air; the air coming in contact with the excessively cold hydrogen vapour is suddenly solidified, and a part of it falls into the liquid hydrogen, causing more rapid evaporation, thereby intensifying the cloud condensation. After the mist has disappeared and all the liquid hydrogen gone, the cup contains a white deposit of solid air. This shortly melts, and on allowing the nitrogen to boil off, the presence of oxygen can be shown by the ignition of a red-hot splinter of wood. Such effects are easily understood when we remember that the boiling-point

of hydrogen is proportionally as much below the boiling-point of air as the latter is below the ordinary temperature of this room.

In order to observe the individual behaviour of the constituents of the air at temperatures below their ordinary boiling-points it is advantageous to place liquid nitrogen and oxygen in separate vacuum vessels, so connected that they may be simultaneously exhausted, as is represented in Fig. 4. On starting the air-pump both liquids enter into rapid ebullition. As the exhaustion gets higher the temperature of each liquid gets lower and lower, and if the melting-point is finally reached in either liquid it must shortly begin to solidify. This condition is quickly brought about in the case of the vessel A containing the liquid nitrogen, which passes rapidly into the condition of a dense white snow; but no amount of time spent in maintaining a good exhaustion (5 to 10 mm. pressure) has any effect in changing the liquid condition of the oxygen in B. Oxygen in fact remains liquid at temperatures where nitrogen is solid. The snow of solid air produced by the evaporation of liquid hydrogen, in the previous experiment, might thus be made up of solid nitrogen and a liquid rain of oxygen. To show that the temperature of boiling hydrogen solidifies oxygen, some of the latter liquid is placed in a vacuum test-tube O (Fig. 3), and liquid hydrogen H is poured on its surface, when the liquid oxygen is quickly transformed into a clear blue solid ice. Both oxygen and nitrogen, and we shall see later, hydrogen can be changed into the condition of transparent ice as well as into the snowy state. A closed vessel filled with any gas at atmospheric pressure, of such a form that a portion of the surface in the shape of a narrow quill tube, can be cooled in boiling liquid hydrogen like B, Fig. 5, shows condensation of the gas to the solid state; the only exceptions being helium and hydrogen itself. Here are two vessels of the same shape as A, B, Fig. 5. The first contains helium showing no condensation when the part B is cooled; the second is filled with hydrogen, which equally shows no change of state under the conditions of the experiment. It is easy, however, to make the hydrogen vessel show liquefaction. For this purpose the experiment with the hydrogen is repeated, only before doing so the part A is heated to about 300° C. over a Bunsen burner, in order to increase the pressure of gas in the interior to above two atmospheres. Now liquefaction is seen to take place with great facility. No change is produced by similarly increasing the pressure in the helium vessel.

The extraordinary command liquid hydrogen gives us over the transition of state in matter may be best illustrated by the use of a new kind of cryophorus. Wollaston's celebrated instrument operates by forcing the evaporation of water in a closed vessel by condensing its vapour in a part of the receiver at a distance from the fluid, thereby causing a lowering of temperature in the latter until freezing takes place. Hence the name cryophorus or cold-bearer. Instead of using water we may now show that the same principle may be applied to the solidification of nitrogen at a distance, instead of water. The sole difference in this case is that the



FIGS. 1, 2, 3, 4, 5.

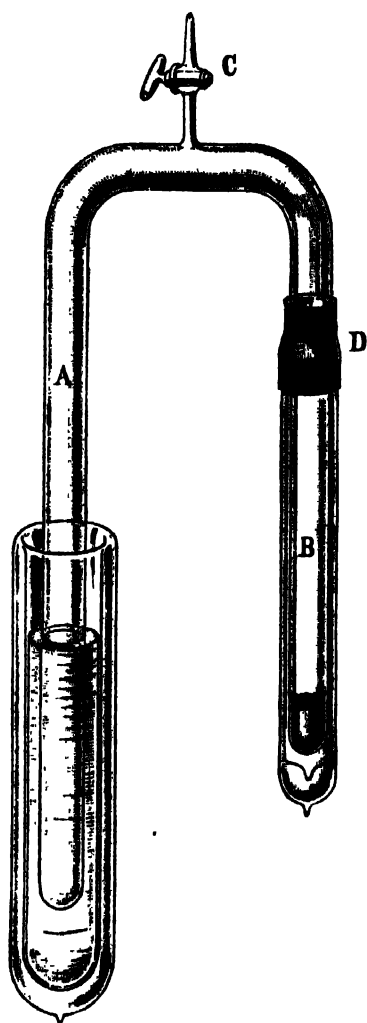
liquid nitrogen must be isolated from the influx of heat by being placed in a vacuum vessel, and the condensation of its vapour must be effected by the use of liquid hydrogen.

No boiling-out operation is necessary with the cryophorus we are about to use. The apparatus is shown in Fig. 6. The vacuum tube B contains liquid nitrogen. It is fitted on by an indiarubber joint to a wide piece of glass tubing doubly bent at right angles, A D; and in order to allow the gas from the boiling liquid to escape before the experiment begins an aperture C is left which can be closed with a stop-cock. On closing C, and inserting a part of the tube A into a vessel containing liquid hydrogen, the gas within is condensed, and thereby the pressure of the vapour in the interior of the vessel is reduced, forcing the liquid nitrogen in the other part of the apparatus to boil with great violence. In a few minutes the temperature of the nitrogen is so much reduced that it passes into the solid state. Many other liquid gases might be used to replace the nitrogen in this experiment. In making a selection, however, it is necessary to take only those bodies that possess a reasonably high tension of vapour at the melting point. The process would not succeed easily with a substance like oxygen, that has no measurable tension of vapour in the solid condition.

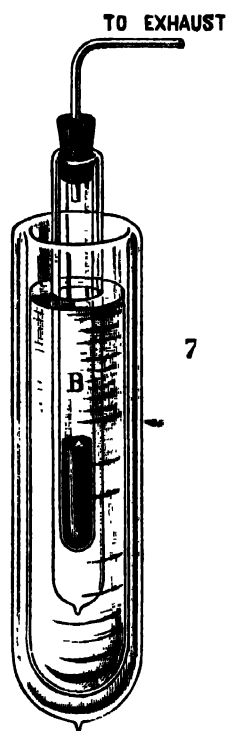
In the autumn of 1898, after the production of liquid hydrogen was possible on a small scale, its solidification was attempted by boiling under reduced pressure. At this time, to make the isolation of the hydrogen as effective as possible, the liquid was placed in a small vacuum test-tube, placed in a larger vessel of the same kind. Excess of hydrogen partly filled the annular space between the two vacuum vessels. On diminishing the pressure by exhaustion the evaporation was mainly thrown on the liquid hydrogen in the annular space between the tubes. In this arrangement the outside surface of the smaller tube was kept at the same temperature as the inside, so that the liquid hydrogen for the time was effectually guarded from influx of heat. With such a combination the liquid hydrogen was evaporated under diminished pressure, yet no solidification took place. Seeing experiments of this kind required a large supply of the liquid, other problems were attacked, and further attempts in the direction of producing the solid for the time abandoned. During the course of the present year many varieties of electric resistance thermometers have been under observation, and with some of these the reduction of temperature brought about by exhaustion was investigated. Thermometers constructed of platinum and platinum-rhodium (alloy) were only lowered  $1\frac{1}{2}^{\circ}$  C. by exhaustion of the liquid hydrogen, and they all gave a boiling-point of  $-245^{\circ}$  C., whereas the reduction in temperature by evaporation *in vacuo* ought to be  $5^{\circ}$  C., and the true boiling-point from  $-252^{\circ}$  C. to  $-253^{\circ}$  C. In the course of these experiments it was noted that almost invariably a slight leak of air occurred which became apparent by its being frozen into an air-snow in the interior of the vessel, where it met the cold vapour of hydrogen. When conducting wires covered with silk have to pass

through indiarubber corks it is very difficult at these excessively low temperatures to prevent leaks, when corks get as hard as a stone, and cements crack in all directions. The effect of this slight air leak on the liquid hydrogen when the pressure got reduced below 60 mm., was very remarkable, as it suddenly solidified into a white froth-like mass like frozen foam. My first notion was that this body might be a sponge of solid air containing liquid hydrogen. The ordinary solid air obtained by evaporation *in vacuo* is a magma of solid nitrogen containing liquid oxygen. The fact, however, that this white solid froth evaporated completely at the low pressure without leaving any substantial amount of solid air led to the conclusion that the body after all must be solid hydrogen. This surmise was confirmed by observing that if the pressure, and therefore the temperature, of the hydrogen was allowed to rise, the solid melted when the pressure reached about 55 mm. The failure of the early experiment must then have been due to supercooling of the liquid, which presumably is prevented by contact with metallic wires and traces of solid air. On the other hand, it is possible the pressure under which the ebullition took place might never have been low enough to reach the solid state.

For the lecture demonstration of solid hydrogen the apparatus may be most conveniently arranged as is shown in Fig. 7. The small vacuum tube B, after being filled with liquid hydrogen, is immersed in a larger vessel of the same kind filled with liquid air. By this arrangement the rate of the liquid hydrogen evaporation is so much diminished that it does not exceed that of liquid air in the same vessel when used in the ordinary way. On gradually applying exhaustion to the liquid hydrogen it is forced from its effective heat isolation to pass to a lower temperature, and when the exhaustion reaches 50 mm. the mass suddenly begins to solidify into a froth-like material. In order to ascertain the appearance of the hydrogen, made by cooling the liquid produced in a hermetically closed vessel the following experiment was arranged. A flask of about a litre capacity, to which a long glass tube was sealed, A B, Fig. 5, was filled with pure dry hydrogen and sealed off. The lower portion B of this tube was calibrated. It was surrounded with liquid hydrogen placed in a vacuum vessel arranged for exhaustion. As soon as the pressure of the boiling hydrogen got well reduced below that of the atmosphere, perfectly clear liquid hydrogen began to collect in the tube B, and could be observed accumulating until the liquid hydrogen surrounding the outside of the tube suddenly passed into a solid white foam-like mass, almost filling the whole space. As it was not possible to see the condition of the hydrogen in the interior of the tube B when it was covered with a large quantity of this solid, the whole apparatus was turned upside down in order to see whether any liquid would run down from B into the flask A. Liquid did not flow down the tube, so the liquid hydrogen with which the tube was partly filled, must have solidified. By placing a strong light on the side of the vacuum test-tube opposite the eye, and maintaining the exhaustion at about 25 mm., gradually



6.



FIGS. 6, 7.

the hydrogen froth became less opaque, and the solid hydrogen in the tube B was seen to be a transparent ice, but the surface looked frothy. This fact prevented the solid density from being determined, but the maximum fluid density has been approximately ascertained. This was found to be 0.086, the liquid at its boiling-point having the density 0.07. The solid hydrogen melts when the pressure of the saturated vapour reaches about 55 mm. In order to determine the temperature of solidification two constant volume hydrogen thermometers were used. One at 0° C. contained hydrogen under a pressure of 269.8 mm., and the other under a pressure of 127 mm. The mean temperature of the solid was found to be 16° absolute under a pressure of 35 mm. All the attempts made to get an accurate electric resistance thermometer for such low temperature observations have been so far unsatisfactory. Now that pure helium is definitely proved to be more volatile than hydrogen, this body, after passing through a spiral glass tube immersed in solid hydrogen to separate all other gases, must be compared with the hydrogen thermometer. Taking the boiling-point as 21° absolute under 760 mm., and the similar value under 35 mm. is 16° absolute, then the following approximate formula for the vapour tension of liquid hydrogen below one atmosphere is derived :—

$$\log p = 6.7341 - 83.28 / T \text{ mm.},$$

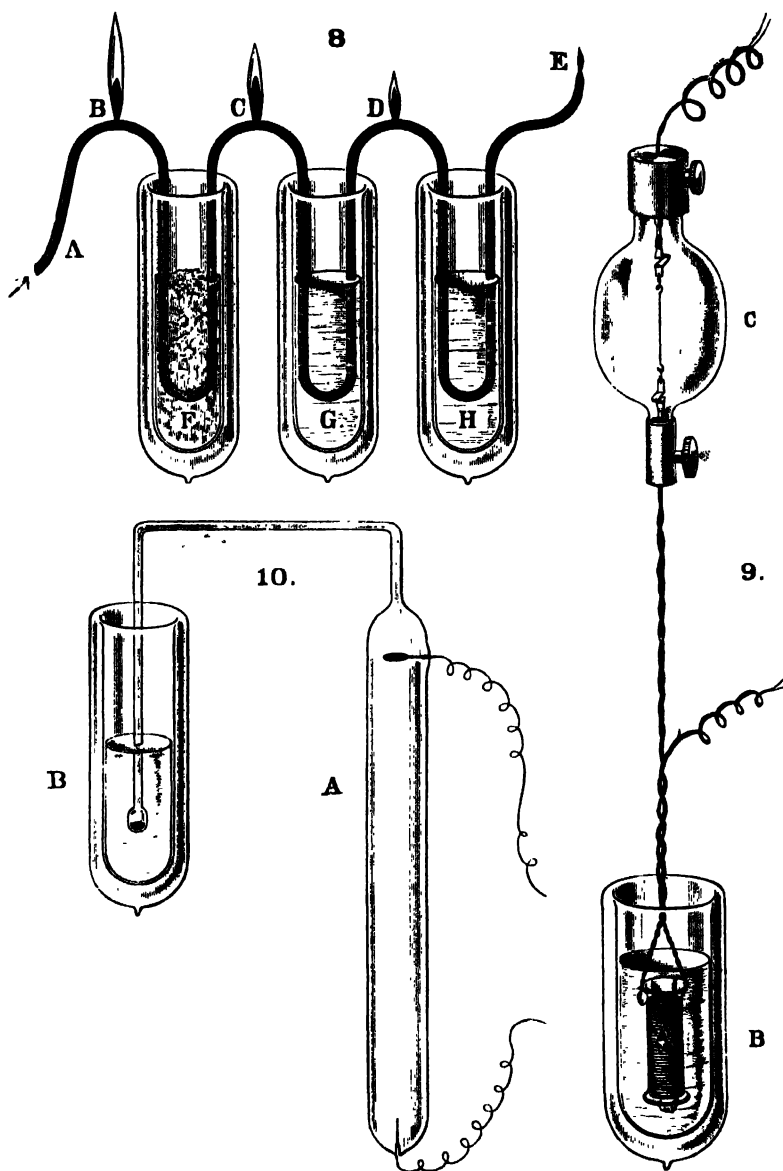
where T is the absolute temperature, and p the pressure in mm. This formula gives for 55 mm. a temperature of 16.7° absolute. The melting-point of hydrogen must therefore be about 16° or 17° absolute. It has to be noted that the pressure in the constant volume hydrogen thermometer, used to determine the temperature of solid hydrogen boiling under 35 mm., had been so far reduced that the measurements were made under from one-half to one-fourth the saturation pressure for the temperature. When the same thermometers were used to determine the boiling-point of hydrogen at atmospheric pressure, the internal gas pressure was only reduced to one-thirteenth the saturation pressure for the temperatures. The absolute accuracy of the boiling-points under diminished pressure must be examined in some future paper. The practical limit of temperature we can command by the evaporation of solid hydrogen is from 14° to 15° absolute. In passing it may be noted that the critical temperature of hydrogen being 30° to 32° absolute, the melting-point is about half the critical temperature. The melting-point of nitrogen is also about half its critical temperature. The foam-like appearance of the solid when produced in an ordinary vacuum vessel is due to the small density of the liquid, and the fact that rapid ebullition is substantially taking place in the whole mass of liquid. The last doubt as to the possibility of solid hydrogen having a metallic character has been removed, and for the future, hydrogen must be classed among the non-metallic elements.

All solid bodies by themselves make very unsatisfactory cooling agents unless we can use them to cool some liquid. Now, with solid hydrogen we can cool no liquid other than hydrogen, so that, for

effective cooling, we must use the liquid just above its freezing-point, which is about  $16^{\circ}$ . It will, however, take a long time to exhaust the wide field of investigation which the use of liquid hydrogen opens up; so we may proceed to illustrate some of its further applications. In former lectures the relation of electrical resistance to temperature has been discussed, and it was experimentally demonstrated that the curves of resistance of the pure metals all pointed to this quality disappearing or becoming exceedingly small at the absolute zero. This fact has been confirmed, even with the most highly conducting metals, down to the lowest temperature we can command. The experiment illustrated in Fig. 9 shows to an audience the diminution of resistance of pure copper wire when cooled in liquid hydrogen, in contrast to liquid air. An incandescent lamp C has been placed in circuit with a fine coil of copper wire A, immersed in liquid air, the resistances being so adjusted that the filament in C is just visible when the current passes under these conditions. Now, on removing the coil from the liquid-air vessel and placing it in another similar vessel filled with liquid hydrogen, a great increase in the brilliancy of the lamp is observed. As a matter of fact, the sample of copper has its resistance in liquid air reduced to about one-twentieth of what it is at the temperature of melting ice, whereas in liquid hydrogen the resistance is reduced to one-hundredth of the same amount. In other words, the resistance in liquid hydrogen is only about one-fifth of what it is in liquid air. The interesting point, however, is that theoretically we should infer, from experiments made at higher temperatures, that at a temperature of  $-223^{\circ}$  C. the copper should have no resistance, or it should have become a perfect conductor. As this is not the case, even at the temperature of  $-253^{\circ}$ , we must infer that the curve co-relating resistance and temperature tends to become asymptotic at the lowest temperatures.

Liquid hydrogen is a most useful agent for the production of high vacua and for the separation of gases from air that may be more volatile than oxygen or nitrogen. An experiment illustrating the production of a high vacuum is shown in Fig. 10 where A is the large electric discharging tube to which has been attached a narrow glass tube twice bent at right angles, and terminating in a bulb at the end for immersion in the liquid hydrogen. The rapidity with which the vacuum is attained is shown by the rate at which the striation in the tube changes and the phosphorescent state supervenes. Another rough illustration of the application of cold to effect the separation of a complex mixture of gases is shown in Fig. 8. Coal-gas is passed in succession through the U-tubes F, G and H made of ordinary gas-pipe, having small holes at B, C, D and E, in order that a flame may be produced before and after each vessel is passed. Each of the U-tubes is placed in a vacuum vessel, and the first cooling substance the gas, in its transit meets is solid carbonic acid in F, then liquid air in G, and finally liquid hydrogen in H. At the temperature of the carbonic acid bath, all the easily condensable hydro-





FIGS. 8, 9, 10.

carbons separate, and consequently the flame C is less luminous than B. The liquid air bath condenses the ethylene and a large part of the marsh gas, and allows the carbonic oxide and the hydrogen to pass through so that flame D is less luminous than C. Finally, after the liquid hydrogen bath, nothing escapes condensation but free hydrogen, the carbonic oxide and any marsh gas being solidified; the result is, the flame E is almost invisible.

A really practical application of liquid hydrogen is the purification of helium obtained from the gases emitted by the mineral springs of Bath. Although the helium only amounts to one-thousandth part by volume—the nine hundred and ninety-nine being chiefly nitrogen—yet the low temperature method of separation can be successfully applied.

Now that we know definitely the approximate values of some of the more important physical constants of liquid hydrogen, it is interesting to look back at the values that have been deduced—say for such a constant as the density—by various workers using entirely different methods. The following table gives some of the more important values of the density of hydrogen under the different conditions in which it enters into organic and inorganic bodies.

#### DENSITY OF HYDROGEN IN DIFFERENT CONDITIONS.

Kopp .. ..	Organic bodies .. ..	0.18
Amagat .. ..	Limit of gaseous compression	0.12
Wroblewski ..	Van der Waals' equation	0.027 (critical density)
Van der Waals	Superior limit of density	0.82
Graham .. ..	Palladium alloy .. ..	2.0
Dewar .. ..	Palladium alloy .. ..	0.63
Dewar .. ..	Liquid hydrogen at B.P.	0.07

My density at the boiling-point agrees substantially with that which can be deduced from Wroblewski's form of the Van der Waals' equation. The deduced densities of Kopp for organic bodies and Amagat for gaseous compression are both about the same value, and may be taken as a mean to be twice the observed density of hydrogen in the liquid state. The conclusions of Graham and myself, touching the density of the hydrogen in the so-called alloy of palladium, must be regarded as altogether exceptional. Even my value would exceed the density of the stuff constituting the real gas molecule, according to the theory of Van der Waals. In order to harmonise the palladium hydrogen results with those deduced from the study of organic bodies, we must assume that, during the formation of the so-called hydrogenium, a condensation of the palladium sufficient to increase its density by one-fifth must take place. This is by no means an unreasonable hypothesis. The mode of determining the density of hydrogen at its melting-point has been previously described and found to be 0.086. In the same way the approximate values for the densities of nitrogen and oxygen at their melting-points have been found, their respective values being 1.07 and 1.27. The following table shows the comparison between my results and those given by Amagat for high gaseous compressions:—

## DENSITIES.

—	Liquid Melting-point.	Gas, 3000 Atmospheres.	Limiting Value, 4000 Atmospheres.
Hydrogen .. ..	0.086	0.097	0.12
Nitrogen .. ..	1.1	0.833	0.12
Oxygen .. ..	1.27	1.127	1.25

It will be noted that the density of gaseous hydrogen at 3000 atmospheres is actually greater than the maximum density of the liquid state; but neither in the case of nitrogen nor oxygen does the density at the same pressure reach the fluid density. Amagat's limiting value for oxygen under 4000 atmospheres would, however, be almost identical with mine.

During the course of my inquiries sufficient data have been accumulated to construct Waterston Formulæ giving the approximate densities of liquid hydrogen, nitrogen and oxygen in each case through a wide range of temperature. The equation for each substance is given in the following table:—

## LIQUID ATOMIC VOLUMES.

$$\begin{aligned}\text{Hydrogen} &= 23.3 - .8.64 \log (32^\circ - t) \\ \text{Nitrogen} &= 30.0 - 11.00 \log (127^\circ - t) \\ \text{Oxygen} &= 32.6 - 10.22 \log (155^\circ - t)\end{aligned}$$

		Absolute Zero.	Observed at Melting-point.
1. Atomic volume of hydrogen	..	10.3	11.7
2. " "	..	12.8	13.1
3. " nitrogen	..	10.20	12.6
4. " oxygen..	..		

From these formulæ we find the respective hypothetical atomic volumes of hydrogen, nitrogen and oxygen at the absolute zero to be 10.3; 12.8 and 10.2. My observed minimum fluid volumes were 11.7; 13 and 12.6. The coefficients of expansion of the liquids, taken in the same order at their respective boiling-points are 0.024; 0.0056 and 0.0046. Thus liquid hydrogen has a coefficient of expansion five times greater than that of liquid oxygen. Further inquiry will enable the constants in these equations to be determined with greater accuracy. In the meantime, however, they give us general ideas of the order of magnitude of the quantities involved.

I have to thank Mr. Robert Lennox for efficient aid in the arrangement and execution of the difficult experiments you have witnessed. Mr. Heath has also heartily assisted in the preparations.

[J. D.]

Friday, April 27, 1900.

SIR FREDERICK BRAMWELL, BART., D.C.L. LL.D. F.R.S.,  
Vice-President, in the Chair.

The Right Hon. LORD KELVIN, G.C.V.O. D.C.L.  
LL.D. F.R.S. *M.R.I.*

*Nineteenth Century Clouds over the Dynamical Theory of  
Heat and Light.*

[In the present article, the substance of the lecture is reproduced—with large additions, in which work commenced at the beginning of last year and continued after the lecture, during thirteen months up to the present time, is described—with results confirming the conclusions and largely extending the illustrations which were given in the lecture. I desire to take this opportunity of expressing my obligations to Mr. William Anderson, my secretary and assistant, for the mathematical tact and skill, the accuracy of geometrical drawing, and the unfailingly faithful perseverance in the long-continued and varied series of drawings and algebraic and arithmetical calculations, explained in the following pages. The whole of this work, involving the determination of results due to more than five thousand individual impacts, has been performed by Mr. Anderson.—K., Feb. 2, 1901.]

§ 1. The beauty and clearness of the dynamical theory, which asserts heat and light to be modes of motion, is at present obscured by two clouds. I. The first came into existence with the undulatory theory of light, and was dealt with by Fresnel and Dr. Thomas Young; it involved the question, How could the earth move through an elastic solid, such as essentially is the luminiferous ether? II. The second is the Maxwell-Boltzmann doctrine regarding the partition of energy.

§ 2. CLOUD I.—RELATIVE MOTION OF ETHER AND PONDERABLE BODIES; such as movable bodies at the earth's surface, stones, metals, liquids, gases; the atmosphere surrounding the earth; the earth itself as a whole; meteorites, the moon, the sun, and other celestial bodies. We might imagine the question satisfactorily answered, by supposing ether to have practically perfect elasticity for the exceedingly rapid vibrations, with exceedingly small extent of distortion, which constitute light; while it behaves almost like a fluid of very small viscosity, and yields with exceedingly small resistance, practically no resistance, to bodies moving through it as slowly as even the most rapid of the heavenly bodies. There are, however, many very serious objections

to this supposition; among them one which has been most noticed, though perhaps not really the most serious, that it seems incompatible with the known phenomena of the aberration of light. Referring to it, Fresnel, in his celebrated letter \* to Arago, wrote as follows:

"Mais il paraît impossible d'expliquer l'aberration des étoiles dans cette hypothèse; je n'ai pu jusqu'à présent du moins concevoir nettement ce phénomène qu'en supposant que l'éther passe librement au travers du globe, et que la vitesse communiquée à ce fluide subtil n'est qu'une petite partie de celle de la terre; n'en excède pas le centième, par exemple.

"Quelque extraordinaire que paraisse cette hypothèse au premier abord, elle n'est point en contradiction, ce me semble, avec l'idée que les plus grands physiciens se sont faite de l'extrême porosité des corps."

The same hypothesis was given by Thomas Young, in his celebrated statement that ether passes through among the molecules or atoms of material bodies like wind blowing through a grove of trees. It is clear that neither Fresnel nor Young had the idea that the ether of their undulatory theory of light, with its transverse vibrations, is essentially an elastic solid, that is to say, matter which resists change of shape with permanent or sub-permanent force. If they had grasped this idea, they must have noticed the enormous difficulty presented by the laceration which the ether must experience if it moves through pores or interstices among the atoms of matter.

§ 3. It has occurred to me that, without contravening anything we know from observation of nature, we may simply deny the scholastic axiom that two portions of matter cannot jointly occupy the same space, and may assert, as an admissible hypothesis, that ether does occupy the same space as ponderable matter, and that ether is not displaced by ponderable bodies moving through space occupied by ether. But how then could matter act on ether, and ether act on matter, to produce the known phenomena of light (or radiant heat), generated by the action of ponderable bodies on ether, and acting on ponderable bodies to produce its visual, chemical, phosphorescent, thermal, and photographic effects? There is no difficulty in answering this question if, as it probably is, ether is a compressible and dilatable † solid. We have only to suppose that the atom exerts force on the ether, by which condensation or rarefaction is produced within the space occupied by the atom. At present ‡ I confine myself,

\* 'Annales de Chimie,' 1818; quoted in full by Larmor in his recent book, 'Ether and Matter,' pp. 320-322.

† To deny this property is to attribute to ether infinitely great resistance against forces tending to condense it or to dilate it—which seems, in truth, an infinitely difficult assumption.

‡ Further developments of the suggested idea have been contributed to the Royal Society of Edinburgh, and to the Congrès International de Physique, held in Paris in August. (Proc. R.S.E. July 1900; vol. of reports, in French, of the Cong. Inter.; and Phil. Mag., Aug., Sept., 1900.)

for the sake of simplicity, to the suggestion of a spherical atom producing condensation and rarefaction, with concentric spherical surfaces of equal density, but the same total quantity of ether within its boundary as the quantity in an equal volume of free undisturbed ether.

§ 4. Consider now such an atom given at rest anywhere in space occupied by ether. Let force be applied to it to cause it to move in any direction, first with gradually increasing speed, and after that with uniform speed. If this speed is anything less than the velocity of light, the force may be mathematically proved to become zero at some short time after the instant when the velocity of the atom becomes uniform, and to remain zero for ever thereafter. What takes place is this:

§ 5. During all the time in which the velocity of the atom is being augmented from zero, two sets of non-periodic waves, one of them equi-voluminal, the other irrotational (which is therefore condensational-rarefactional), are being sent out in all directions through the surrounding ether. The rears of the last of these waves leave the atom, at some time after its acceleration ceases. This time, if the motion of the ether outside the atom, close beside it, is infinitesimal, is equal to the time taken by the slower wave (which is the equi-voluminal) to travel the diameter of the atom, and is the short time referred to in § 4. When the rears of both waves have got clear of the atom, the ether within it and in the space around it, left clear by both rears, has come to a steady state of motion relatively to the atom. This steady motion approximates more and more nearly to uniform motion in parallel lines, at greater and greater distances from the atom. At a distance of twenty diameters it differs exceedingly little from uniformity.

§ 6. But it is only when the velocity of the atom is very small in comparison with the velocity of light, that the disturbance of the ether in the space close round the atom is infinitesimal. The propositions asserted in § 4 and the first sentence of § 5 are true, however little the final velocity of the atom falls short of the velocity of light. If this uniform final velocity of the atom exceeds the velocity of light, by ever so little, a non-periodic conical wave of equi-voluminal motion is produced, according to the same principle as that illustrated for sound by Mach's beautiful photographs of illumination by electric spark, showing, by changed refractivity, the condensational-rarefactional disturbance produced in air by the motion through it of a rifle bullet. The semi-vertical angle of the cone, whether in air or ether, is equal to the angle whose sine is the ratio of the wave velocity to the velocity of the moving body.\*

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\* On the same principle we see that a body moving steadily (and, with little error, we may say also that a fish or water-fowl propelling itself by fins or web-feet) through calm water, either floating on the surface or wholly submerged at some moderate distance below the surface, produces no wave disturbance if its

§ 7. If, for a moment, we imagine the steady motion of the atom to be at a higher speed than the wave velocity of the condensational-rarefactional wave, two conical waves, of angles corresponding to the two wave velocities, will be steadily produced; but we need not occupy ourselves at present with this case, because the velocity of the condensational-rarefactional wave in ether is, we are compelled to believe, enormously great in comparison with the velocity of light.

§ 8. Let now a periodic force be applied to the atom so as to cause it to move to and fro continually, with simple harmonic motion. By the first sentence of § 5 we see that two sets of periodic waves, one equi-voluminal, the other irrotational, are continually produced. Without mathematical investigation we see that if, as in ether, the condensational-rarefactional wave velocity is very great in comparison with the equi-voluminal wave velocity, the energy taken by the condensational-rarefactional wave is exceedingly small in comparison with that taken by the equi-voluminal wave; how small we can find easily enough by regular mathematical investigation. Thus we see how it is that the hypothesis of § 3 suffices for the answer suggested in that section to the question, How could matter act on ether so as to produce light?

§ 9. But this, though of primary importance, is only a small part

velocity is less than the minimum wave velocity due to gravity and surface tension (being about 23 cms. per second, or '44 of a nautical mile per hour, whether for sea water or fresh water); and if its velocity exceeds the minimum wave velocity, it produces a wave disturbance bounded by two lines inclined on each side of its wake at angles each equal to the angle whose sine is the minimum wave velocity divided by the velocity of the moving body. It is easy for anyone to observe this by dipping vertically a pencil or a walking stick into still water in a pond (or even in a good-sized hand basin), and moving it horizontally, first with exceeding small speed, and afterwards faster and faster. I first noticed it nineteen years ago, and described observations for an experimental determination of the minimum velocity of waves, in a letter to William Froude, published in 'Nature' for October 26, and in the Phil. Mag. for November 1871, from which the following is extracted. "[Recently, in the schooner yacht *Lalla Rookh*], "being becalmed in the Sound of Mull, I had an excellent opportunity, with the "assistance of Professor Helmholtz, and my brother from Belfast [the late "Professor James Thomson], of determining by observation the minimum wave- "velocity with some approach to accuracy. The fishing-line was hung at a distance "of two or three feet from the vessel's side, so as to cut the water at a point not "sensibly disturbed by the motion of the vessel. The speed was determined by "throwing into the sea pieces of paper previously wetted, and observing their "times of transit across parallel planes, at a distance of 912 centimetres asunder, "fixed relatively to the vessel by marks on the deck and gunwale. By watching "carefully the pattern of ripples and waves which connected the ripples in "front with the waves in rear, I had seen that it included a set of parallel waves "slanting off obliquely on each side and presenting appearances which proved "them to be waves of the critical length and corresponding minimum speed of "propagation." When the speed of the yacht fell to but little above the critical "velocity, the front of the ripples was very nearly perpendicular to the line of "motion, and when it just fell below the critical velocity the ripples disappeared "altogether, and there was no perceptible disturbance on the surface of the water. "The sea was "glassy"; though there was wind enough to propel the schooner "at speed varying between  $\frac{1}{2}$  mile and 1 mile per hour.

of the very general question pointed out in § 3 as needing answer. Another part, fundamental in the undulatory theory of optics, is, How is it that the velocity of light is smaller in transparent ponderable matter than in pure ether? Attention was called to this particular question in my address to the Royal Institution, of last April; and a slight explanation of my proposal for answering it was given, and illustrated by a diagram. The validity of this proposal is confirmed by a somewhat elaborate discussion and mathematical investigation of the subject worked out since that time and communicated under the title, 'On the Motion produced in an Infinite Elastic Solid by the Motion through the Space occupied by it of a Body acting on it only by Attraction or Repulsion,' to the Royal Society of Edinburgh on July 17, and to the Congrès International de Physique for its meeting at Paris in the beginning of August.

§ 10. The other phenomena referred to in § 3 come naturally under the general dynamics of the undulatory theory of light, and the full explanation of them all is brought much nearer if we have a satisfactory fundamental relation between ether and matter, instead of the old intractable idea that atoms of matter displace ether from the space before them, when they are in motion relatively to the ether around them. May we then suppose that the hypothesis which I have suggested clears away the first of our two clouds? It certainly would explain the "aberration of light" connected with the earth's motion through ether in a thoroughly satisfactory manner. It would allow the earth to move with perfect freedom through space occupied by ether without displacing it. In passing through the ether, an elastic solid, would not be lacerated as it would be according to Fresnel's idea of porosity and ether moving through the pores as if it were a fluid. Ether would move relatively to ponderables with the perfect freedom wanted for what we know of aberration, instead of the imperfect freedom of air moving through a grove of trees suggested by Thomas Young. According to it, and for simplicity neglecting the comparatively very small component due to the earth's rotation (only  $\cdot 46$  of a kilometre per second at the equator where it is a maximum), and neglecting the imperfectly known motion of the solar system through space towards the constellation Hercules, discovered by Herschel,\* there would be at all points of the earth's surface a flow

\* The splendid spectroscopic method originated by Huggins thirty-three years ago, for measuring the component in the line of vision of the relative motion of the earth, and any visible star, has been carried on since that time with admirable perseverance and skill by other observers, who have from their results made estimates of the velocity and direction of the motion through space of the centre of inertia of the solar system. My Glasgow colleague, Professor Becker, has kindly given me the following information on the subject of these researches:

"The early (1888) Potsdam photographs of the spectra of 51 stars brighter than 2 $\frac{1}{2}$  magnitude have been employed for the determination of the apex and velocity of the solar system. Kempf (*Astronomische Nachrichten*, vol. 132) finds for the apex: right ascension,  $206^{\circ} \pm 12^{\circ}$ ; declination,  $46^{\circ} \pm 9^{\circ}$ ; velocity, 19 kilometres per second; and Risteen (*Astronomical Journal*, 1893) finds practically the same



of ether at the rate of 80 kilometres per second in lines all parallel to the tangent to the earth's orbit round the sun. There is nothing inconsistent with this in all we know of the ordinary phenomena of terrestrial optics; but, alas! there is inconsistency with a conclusion that ether in the earth's atmosphere is motionless relatively to the earth, seemingly proved by an admirable experiment designed by Michelson, and carried out, with most searching care to secure a trustworthy result, by himself and Morley.\* I cannot see any flaw either in the idea or in the execution of this experiment. But a possibility of escaping from the conclusion which it seemed to prove, may be found in a brilliant suggestion made independently by Fitzgerald † and by Lorentz ‡ of Leyden, to the effect that the motion of ether through matter may slightly alter its linear dimensions, according to which if the stone slab constituting the sole plate of Michelson and Morley's apparatus has, in virtue of its motion through space occupied by ether, its lineal dimensions shortened one one-hundred-millionth || in the direction of motion, the result of the experiment would not disprove the free motion of ether through space occupied by the earth.

§ 11. I am afraid we must still regard Cloud No. I. as very dense.

§ 12. CLOUD II.—Waterston (in a communication to the Royal Society, now famous, which, after lying forty-five years buried and almost forgotten in the archives, was rescued from oblivion by Lord Rayleigh and published, with an introductory notice of great interest and importance, in the Transactions of the Royal Society for 1892) enunciated the following proposition: "In mixed media the mean square molecular velocity is inversely proportional to the specific weight of the molecule. This is the law of the equilibrium of vis viva." Of this proposition Lord Rayleigh in a footnote ¶ says, "This is the first statement of a very important theorem (see also Brit. Assoc. Rep., 1851). The demonstration, however, of § 10 can hardly be defended. It bears some resemblance to an argument indicated and exposed by Professor Tait (Edinburgh Trans., vol. 33, p. 79, 1886). There is reason to think that this law is intimately connected with the Maxwellian distribution of velocities of which Waterston had no knowledge."

§ 13. In Waterston's statement, the "specific weight of a mole-

quantities. The proper motions of the fixed stars assign to the apex a position which may be anywhere in a narrow zone parallel to the Milky-way, and extending  $20^\circ$  on both sides of a point of Right Ascension  $275^\circ$  and Declination  $+30^\circ$ . The authentic mean of 13 values determined by the methods of Argelander or Airy gives  $274^\circ$  and  $+33^\circ$  (André, 'Traité d'Astronomie Stellaire')."

\* Phil. Mag., December 1887.

† Public Lectures in Trinity College, Dublin.

‡ Versuch einer Theorie der electrischen und optischen Erscheinungen in bewegten Körpern.

|| This being the square of the ratio of the earth's velocity round the sun (80 kilometres per sec.) to the velocity of light (300,000 kilometres per sec.).

¶ Phil. Trans. A, 1892, p. 16.

cule" means what we now call simply the mass of a molecule; and "molecular velocity" means the translational velocity of a molecule. Writing on the theory of sound in the *Phil. Mag.* for 1858, and referring to the theory developed in his buried paper,\* Waterston said, "The theory . . . assumes . . . that if the impacts produce "rotatory motion the vis viva thus invested bears a constant ratio to "the rectilineal vis viva." This agrees with the very important principle or truism given independently about the same time by Clausius to the effect that the mean energy, kinetic and potential, due to the relative motion of all the parts of any molecule of a gas, bears a constant ratio to the mean energy of the motion of its centre of inertia when the density and pressure are constant.

§ 14. Without any knowledge of what was to be found in Waterston's buried paper, Maxwell, at the meeting of the British Association at Aberdeen, in 1859 † gave the following proposition regarding the motion and collisions of perfectly elastic spheres: "Two systems of "particles move in the same vessel; to prove that the mean vis viva "of each particle will become the same in the two systems." This is precisely Waterston's proposition regarding the law of partition of energy, quoted in § 12 above; but Maxwell's 1860 proof was certainly not more successful than Waterston's. Maxwell's 1860 proof has always seemed to me quite inconclusive, and many times I urged my colleague, Professor Tait, to enter on the subject. This he did, and in 1886 he communicated to the Royal Society of Edinburgh a paper ‡ on the foundations of the kinetic theory of gases, which contained a critical examination of Maxwell's 1860 paper, highly appreciative of the great originality and splendid value, for the kinetic theory of gases, of the ideas and principles set forth in it; but showing that the demonstration of the theorem of the partition of energy in a mixed assemblage of particles of different masses was inconclusive, and successfully substituting for it a conclusive demonstration.

§ 15. Waterston, Maxwell, and Tait, all assume that the particles of the two systems are thoroughly mixed (Tait, § 18), and their theorem is of fundamental importance in respect to the specific heats of mixed gases. But they do not, in any of the papers already referred to, give any indication of a proof of the corresponding theorem, regarding the partition of energy between two sets of equal particles separated by a membrane impermeable to the molecules, while permitting forces to act across it between the molecules on its two sides, ||

\* 'On the Physics of Media that are Composed of Force and Perfectly Elastic Molecules in a State of Motion.' *Phil. Trans. A*, 1892, p. 13.

† 'Illustrations of the Dynamical Theory of Gases.' *Phil. Mag.*, January and July 1860, and collected works, vol. i. p. 378.

‡ *Phil. Trans. R.S.E.*, 'On the Foundations of the Kinetic Theory of Gases,' May 14 and December 6, 1886, and January 7, 1887.

|| A very interesting statement is given by Maxwell regarding this subject in his latest paper regarding the Boltzmann-Maxwell doctrine. 'On Boltzmann's Theorem on the Average Distribution of Energy in a System of Material Points,' *Camb. Phil. Trans.*, May 6, 1878; *Collected Works*, vol. ii. pp. 713-741.

which is the simplest illustration of the molecular dynamics of Avogadro's law. It seems to me, however, that Tait's demonstration of the Waterston-Maxwell law may possibly be shown to virtually include, not only this vitally important subject, but also the very interesting, though comparatively unimportant, case of an assemblage of particles of equal masses with a single particle of different mass moving about among them.

§ 16. In §§ 12, 14, 15, "particle" has been taken to mean what is commonly, not correctly, called an elastic sphere, but what is in reality a Boscovich atom acting on other atoms in lines exactly through its centre of inertia (so that no rotation is in any case produced by collisions), with, as law of action between two atoms, *no force at distance greater than the sum of their radii, infinite force at exactly this distance*. None of the demonstrations, unsuccessful or successful, to which I have referred would be essentially altered if, instead of this last condition, we substitute a repulsion increasing with diminishing distance, according to any law for distances less than the sum of the radii, subject only to the condition that it would be infinite before the distance became zero. In fact the impact, oblique or direct, between two Boscovich atoms thus defined, has the same result after the collision is completed (that is to say, when their spheres of action get outside one another) as collision between two conventional elastic spheres, imagined to have radii dependent on the lines and velocities of approach before collision (the greater the relative velocity the smaller the effective radii); and the only assumption essentially involved in those demonstrations is, that the radius of each sphere is very small in comparison with the average length of free path.

§ 17. But if the particles are Boscovich atoms, having centre of inertia not coinciding with centre of force; or quasi Boscovich atoms, of non-spherical figure; or (a more acceptable supposition) if each particle is a cluster of two or more Boscovich atoms: rotations and changes of rotation would result from collisions. Waterston's and Clausius' leading principle, quoted in § 13 above, must now be taken into account, and Tait's demonstration is no longer applicable. Waterston and Clausius, in respect to rotation, both wisely abstained from saying more than that the average kinetic energy of rotation bears a constant ratio to the average kinetic energy of translation. With magnificent boldness Boltzmann and Maxwell declared that the ratio is equality; Boltzmann having found what seemed to him a demonstration of this remarkable proposition, and Maxwell having accepted the supposed demonstration as valid.

§ 18. Boltzmann went further\* and extended the theorem of equality of mean kinetic energies to any system of a finite number of material points (Boscovich atoms) acting on one another, according to any law of force, and moving freely among one another; and finally,

\* 'Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiellen Punkten.' Sitzb. K. Akad. Wien., October 8, 1868.

Maxwell\* gave a demonstration extending it to the generalised Lagrangian co-ordinates of any system whatever, with a finite or infinitely great number of degrees of freedom. The words in which he enunciated his supposed theorem are as follows :

"The only assumption which is necessary for the direct proof is "that the system, if left to itself in its actual state of motion, will, "sooner or later, pass [infinitely nearly †] through every phase which is "consistent with the equation of energy" (p. 714) and, again (p. 716).

"It appears from the theorem, that in the ultimate state of the "system the average ‡ kinetic energy of two portions of the system must "be in the ratio of the number of degrees of freedom of those portions.

"This, therefore, must be the condition of the equality of temperature of the two portions of the system."

I have never seen validity in the demonstration || on which Maxwell founds this statement, and it has always seemed to me exceedingly improbable that it can be true. If true, it would be very wonderful, and most interesting in pure mathematical dynamics. Having been published by Boltzmann and Maxwell it would be worthy of most serious attention, even without consideration of its bearing on thermo-dynamics. But, when we consider its bearing on thermo-dynamics, and in its first and most obvious application we find it destructive of the kinetic theory of gases, of which Maxwell was one of the chief founders, we cannot see it otherwise than as a cloud on the dynamical theory of heat and light.

§ 19. For the kinetic theory of gases, let each molecule be a cluster of Boscovich atoms. This includes every possibility ("dynamical," or "electrical," or "physical," or "chemical") regarding the nature and qualities of a molecule and of all its parts. The mutual forces between the constituent atoms must be such that the cluster is in stable equilibrium if given at rest ; which means, that if started from

\* 'On Boltzmann's Theorem on the Average Distribution of Energy in a System of Material Points.' Maxwell's Collected Papers, vol. ii. pp. 713-741, and Camb. Phil. Trans., May 6, 1878.

† I have inserted these two words as certainly belonging to Maxwell's meaning.—K.

‡ The average here meant is a time-average through a sufficiently long time.

|| The mode of proof followed by Maxwell, and its connection with antecedent considerations of his own and of Boltzmann, imply, as included in the general theorem, that the average kinetic energy of any one of three rectangular components of the motion of the centre of inertia of an isolated system, acted upon only by mutual forces between its parts, is equal to the average kinetic energy of each generalised component of motion relatively to the centre of inertia. Consider, for example, as "parts of the system" two particles of masses  $m$  and  $m'$  free to move only in a fixed straight line, and connected to one another by a massless spring. The Boltzmann-Maxwell doctrine asserts that the average kinetic energy of the motion of the inertial centre is equal to the average kinetic energy of the motion relative to the inertial centre. This is included in the wording of Maxwell's statement in the text if, but not unless,  $m = m'$ . See footnote on § 7 of my paper 'On some Test-Cases for the Boltzmann-Maxwell Doctrine regarding Distribution of Energy.' Proc. Roy. Soc., June 11, 1891.

equilibrium with its constituents in any state of relative motion, no atom will fly away from it, provided the total kinetic energy of the given initial motion does not exceed some definite limit. A gas is a vast assemblage of molecules thus defined, each moving freely through space, except when in collision with another cluster, and each retaining all its own constituents unaltered, or only altered by interchange of similar atoms between two clusters in collision.

§ 20. For simplicity we may suppose that each atom,  $A$ , has a definite radius of activity,  $a$ , and that atoms of different kinds,  $A, A'$ , have different radii of activity,  $a, a'$ ; such that  $A$  exercises no force on any other atom,  $A', A''$ , when the distance between their centres is greater than  $a + a'$  or  $a + a''$ . We need not perplex our minds with the inconceivable idea of "virtue," whether for force or for inertia, residing in a mathematical point \* the centre of the atom; and without mental strain we can distinctly believe that the substance (the "substratum" of qualities) resides, not in a point, nor vaguely through all space, but definitely in the spherical volume of space bounded by the spherical surface whose radius is the radius of activity of the atom, and whose centre is the centre of the atom. In our intermolecular forces thus defined, we have no violation of the old scholastic law, "Matter cannot act where it is not," but we explicitly violate the other scholastic law, "Two portions of matter cannot simultaneously occupy the same space." We leave to gravitation, and possibly to electricity (probably not to magnetism), the at present very unpopular idea of action at a distance.

§ 21. We need not now (as in § 16, when we wished to keep as near as we could to the old idea of colliding elastic globes) suppose the mutual force to become infinite repulsion before the centres of two atoms, approaching one another, meet. Following Boscovich, we may assume the force to vary according to any law of alternate attraction and repulsion, but without supposing any infinitely great force, whether of repulsion or attraction, at any particular distance; but we must assume the force to be zero when the centres are coincident. We may even admit the idea of the centres being absolutely coincident, in at all events some cases of a chemical combination of two or more atoms; although we might consider it more probable that in most cases the chemical combination is a cluster, in which the volumes of the constituent atoms overlap without any two centres absolutely coinciding.

§ 22. The word "collision" used without definition in § 19 may now, in virtue of §§ 20, 21, be unambiguously defined thus: Two atoms are said to be in collision during all the time their volumes overlap after coming into contact. They necessarily in virtue of inertia separate again, unless some third body intervenes with action which causes them to remain overlapping; that is to say,

\* See Math. and Phys. Papers, vol. iii. art. xcvi. 'Molecular Constitution of Matter,' § 14.

causes combination to result from collision. Two clusters of atoms are said to be in collision when, after being separate, some atom or atoms of one cluster come to overlap some atom or atoms of the other. In virtue of inertia the collision must be followed either by the two clusters separating, as described in the last sentence of § 19, or by some atom or atoms of one or both systems being sent flying away. This last supposition is a matter-of-fact statement belonging to the magnificent theory of dissociation, discovered and worked out by Sainte-Clair Deville without any guidance from the kinetic theory of gases. In gases approximately fulfilling the gaseous laws (Boyle's and Charles'), two clusters must in general fly asunder after collision. Two clusters could not possibly remain permanently in combination without at least one atom being sent flying away after collision between two clusters with no third body intervening.\*

§ 23. Now for the application of the Boltzman-Maxwell doctrine to the kinetic theory of gases: consider first a homogeneous single gas, that is, a vast assemblage of similar clusters of atoms moving and colliding as described in the last sentence of § 19; the assemblage being so sparse that the time during which each cluster is in collision is very short in comparison with the time during which it is unacted on by other clusters, and its centre of inertia, therefore, moves uniformly in a straight line. If there are  $i$  atoms in each cluster, it has  $3i$  freedoms to move, that is to say, freedoms in three rectangular directions for each atom. The Boltzman-Maxwell doctrine asserts that the mean kinetic energies of these  $3i$  motions are all equal, whatever be the mutual forces between the atoms. From this, when the durations of the collisions are not included in the time-averages, it is easy to prove algebraically (with exceptions noted below) that the time-average of the kinetic energy of the component translational velocity of the inertial centre, † in any direction, is equal to any one of the  $3i$  mean kinetic energies asserted to be equal to one another in the preceding statement. There are exceptions to the algebraic proof corresponding to the particular exception referred to in the last footnote to § 18 above; but, nevertheless, the general Boltzmann-Maxwell doctrine includes the proposition, even in those cases in which it is not deducible algebraically from the equality of the  $3i$  energies. Thus, without exception, the average kinetic energy of any component of the motion of the inertial centre is, according to the Boltzmann-Maxwell doctrine, equal to  $\frac{1}{3i}$  of the

whole average kinetic energy of the system. This makes the total average energy, potential and kinetic, of the whole motion of the system, translational and relative, to be  $3i(1 + P)$  times the mean

\* See Kelvin's Math. and Phys. Papers, vol. iii. art. xcvi. § 33. In this reference, for "scarcely" substitute "not."

† This expression I use for brevity to signify the kinetic energy of the whole -- ideally collected at the centre of inertia.

kinetic energy of one component of the motion of the inertial centre, where  $P$  denotes the ratio of the mean potential energy of the relative displacements of the parts to the mean kinetic energy of the whole system. Now, according to Clausius' splendid and easily proved theorem regarding the partition of energy in the kinetic theory of gases, the ratio of the difference of the two thermal capacities to the constant-volume thermal capacity is equal to the ratio of twice a single component of the translational energy to the total energy. Hence, if according to our usual notation we denote the ratio of the thermal capacity pressure-constant to the thermal capacity volume-constant by  $k$ , we have,

$$k - 1 = \frac{2}{3i(1 + P)}.$$

§ 24. *Example 1.*—For first and simplest example, consider a monatomic gas. We have  $i = 1$ , and according to our supposition (the supposition generally, perhaps universally, made) regarding atoms, we have  $P = 0$ . Hence,  $k - 1 = \frac{2}{3}$ .

This is merely a fundamental theorem in the kinetic theory of gases for the case of no rotational or vibrational energy of the molecule; in which there is no scope either for Clausius' theorem or for the Boltzmann-Maxwell doctrine. It is beautifully illustrated by mercury vapour, a monatomic gas according to chemists, for which many years ago Kundt, in an admirably designed experiment, found  $k - 1$  to be very approximately  $\frac{2}{3}$ ; and by the newly discovered gases argon, helium, and krypton, for which also  $k - 1$  has been found to have approximately the same value, by Rayleigh and Ramsay. But each of these four gases has a large number of spectrum lines, and therefore a large number of vibrational freedoms, and therefore, if the Boltzmann-Maxwell doctrine were true,  $k - 1$  would have some exceedingly small value, such as that shown in the ideal example of § 26 below. On the other hand, Clausius' *theorem* presents no difficulty; it merely asserts that  $k - 1$  is necessarily less than  $\frac{2}{3}$  in each of these four cases, as in every case in which there is any rotational or vibrational energy whatever; and proves, from the values found experimentally for  $k - 1$  in the four gases, that in each case the total of rotational and vibrational energy is exceedingly small in comparison with the translational energy. It justifies admirably the chemical doctrine that mercury vapour is *practically a monatomic gas*, and it proves that argon, helium, and krypton, are also *practically monatomic*, though none of these gases has hitherto shown any chemical affinity or action of any kind from which chemists could draw any such conclusion.

But Clausius' theorem, taken in connection with Stokes' and Kirchhoff's dynamics of spectrum analysis, throws a new light on what we are now calling a "practically monatomic gas." It shows that, unless we admit that the atoms can be set into rotation or vibration by mutual collisions (a most unacceptable hypothesis), it must have satellites connected with it (or ether condensed into it or around it)

and kept, by the collisions, in motion relatively to it with total energy exceedingly small in comparison with the translational energy of the whole system of atom and satellites. The satellites must in all probability be of exceedingly small mass in comparison with that of the chief atom. Can they be the "ions" by which J. J. Thomson explains the electric conductivity induced in air and other gases by ultra-violet light, Röntgen rays, and Becquerel rays?

Finally, it is interesting to remark that all the values of  $k - 1$  found by Rayleigh and Ramsay are somewhat less than  $\frac{2}{3}$ ; argon  $\cdot 64$ ,  $\cdot 61$ ; helium  $\cdot 652$ ; krypton  $\cdot 666$ . If the deviation from  $\cdot 667$  were accidental they would probably have been some in defect and some in excess.

*Example 2.*—As a next simplest example let  $i = 2$ , and as a very simplest case let the two atoms be in stable equilibrium when concentric, and be infinitely nearly concentric when the clusters move about, constituting a homogeneous gas. This supposition makes  $P = \frac{1}{2}$ , because the average potential energy is equal to the average kinetic energy in simple harmonic vibrations; and in our present case half the whole kinetic energy, according to the Boltzmann-Maxwell doctrine, is vibrational, the other half being translational. We find  $k - 1 = \frac{2}{3} = \cdot 2222$ .

*Example 3.*—Let  $i = 2$ ; let there be stable equilibrium, with the centres C, C' of the two atoms at a finite distance  $a$  asunder, and let the atoms be always very nearly at this distance asunder when the clusters are not in collision. The relative motions of the two atoms will be according to three freedoms, one vibrational, consisting of very small shortenings and lengthenings of the distance CC', and two rotational, consisting of rotations round one or other of two lines perpendicular to each other and perpendicular to CC' through the inertial centre. With these conditions and limitations, and with the supposition that half the average kinetic energy of the rotation is comparable with the average kinetic energy of the vibrations, or exactly equal to it as according to the Boltzmann-Maxwell doctrine, it is easily proved that in rotation the excess of CC' above the equilibrium distance  $a$ , due to centrifugal force, must be exceedingly small in comparison with the maximum value of CC' —  $a$  due to the vibration. Hence the average potential energy of the rotation is negligible in comparison with the potential energy of the vibration. Hence, of the three freedoms for relative motion there is only one contributory to  $P$ , and therefore we have  $P = \frac{1}{3}$ . Thus we find  $k - 1 = \frac{2}{3} = \cdot 2857$ .

The best way of experimentally determining the ratio of the two thermal capacities for any gas is by comparison between the observed and the Newtonian velocities of sound. It has thus been ascertained that, at ordinary temperatures and pressures,  $k - 1$  differs but little from  $\cdot 406$  for common air, which is a mixture of the two gases nitrogen and oxygen, each diatomic according to modern chemical theory; and the greatest value that the Boltzmann-Maxwell doctrine can give for a diatomic gas is the  $\cdot 2857$  of Ex. 3. This notable discrepance



from observation, suffices to absolutely disprove the Boltzmann-Maxwell doctrine. What is really established in respect to partition of energy is what Clausius' theorem tells us (§ 23 above). We find, as a result of observation and true theory, that the average kinetic energy of translation of the molecules of common air is  $\cdot 609$  of the total energy, potential and kinetic, of the relative motion of the constituents of the molecules.

§ 25. The method of treatment of Ex. 3 above, carried out for a cluster of any number of atoms greater than two not in one line,  $j + 2$  atoms, let us say, shows us that there are three translational freedoms; three rotational freedoms, relatively to axes through the inertial centre; and  $3j$  vibrational freedoms. Hence we have  $P = \frac{j}{j+2}$ , and we find  $k - 1 = \frac{1}{3(1+j)}$ . The values of  $k - 1$  thus calculated for a triatomic and tetratomic gas, and calculated as above in Ex. 3 for a diatomic gas, are shown in the following table, and compared with the results of observation for several such gases:

Gas.	Values of $k - 1$	
	According to the B.-M. doctrine.	By Observation.
Air	$\frac{2}{3} = \cdot 2857$	$\cdot 406$
H <sub>2</sub>	" "	$\cdot 40$
O <sub>2</sub>	" "	$\cdot 41$
Cl <sub>2</sub>	" "	$\cdot 32$
CO	" "	$\cdot 39$
NO	" "	$\cdot 39$
CO <sub>2</sub>	$\frac{1}{6} = \cdot 1667$	$\cdot 30$
N <sub>2</sub> O	" "	$\cdot 331$
NH <sub>3</sub>	$\frac{1}{9} = \cdot 1111$	$\cdot 311$

It is interesting to see how the dynamics of Clausius' theorem is verified by the results of observation shown in the table. The values of  $k - 1$  for all the gases are less than  $\frac{2}{3}$ , as they must be when there is any appreciable energy of rotation or vibration in the molecule. They are different for different diatomic gases; ranging from  $\cdot 42$  for oxygen to  $\cdot 32$  for chlorine, which is quite as might be expected, when we consider that the laws of force between the two atoms may differ largely for the different kinds of atoms. The values of  $k - 1$  are, on the whole, smaller for the tetratomic and triatomic than for the diatomic gases, as might be expected from consideration of Clausius' principle. It is probable that the differences of  $k - 1$  for the different diatomic gases are real, although there is considerable uncertainty with regard to the observational results for all or some of the gases other than air. It is certain that

the discrepancies from the values, calculated according to the Boltzmann-Maxwell doctrine, are real and great; and that in each case, diatomic, triatomic, and tetratomic, the doctrine gives a value for  $k - 1$  much smaller than the truth.

§ 26. But, in reality, the Boltzmann-Maxwell doctrine errs enormously more than is shown in the preceding table. Spectrum analysis showing vast numbers of lines for each gas makes it certain that the numbers of freedoms of the constituents of each molecule is enormously greater than those which we have been counting, and therefore that unless we attribute vibratile quality to each individual atom, the molecule of every one of the ordinary gases must have a vastly greater number of atoms in its constitution than those hitherto reckoned in regular chemical doctrine. Suppose, for example, there are forty-one atoms in the molecule of any particular gas; if the doctrine were true, we should have  $j = 39$ . Hence there are 117 vibrational freedoms, so that there might be 117 visible lines in the spectrum of the gas; and we have  $k - 1 = \frac{1}{120} = \cdot 0083$ . There is,

in fact, no possibility of reconciling the Boltzmann-Maxwell doctrine with the truth regarding the specific heats of gases.

§ 27. It is, however, not quite possible to rest contented with the mathematical verdict not proven, and the experimental verdict not true, in respect to the Boltzmann-Maxwell doctrine. I have always felt that it should be mathematically tested by the consideration of some particular case. Even if the theorem were true, stated as it was somewhat vaguely, and in such general terms that great difficulty has been felt as to what it is really meant to express, it would be very desirable to see even one other simple case, besides that original one of Waterston's, clearly stated and tested by pure mathematics. Ten years ago,\* I suggested a number of test cases, some of which have been courteously considered by Boltzmann; but no demonstration either of the truth or untruth of the doctrine as applied to any one of them has hitherto been given. A year later, I suggested what seemed to me a decisive test case disproving the doctrine; but my statement was quickly and justly criticised by Boltzmann and Poincaré; and more recently Lord Rayleigh † has shown very clearly that my simple test case was quite indecisive. This last article of Rayleigh's has led me to resume the consideration of several different classes of dynamical problems, which had occupied me more or less at various times during the last twenty years, each presenting exceedingly interesting features in connection with the double question: Is this a case which admits of the application of the Boltzmann-Maxwell doctrine; and if so, is the doctrine true for it?

\* 'On some Test Cases for the Maxwell-Boltzmann Doctrine regarding Distribution of Energy.' *Proc. Roy. Soc.*, June 11, 1891.

† *Phil. Mag.*, vol. xxxiii. 1892, p. 356. 'Remarks on Maxwell's Investigation respecting Boltzmann's Theorem.'

§ 28. Premising that the mean kinetic energies with which the Boltzmann-Maxwell doctrine is concerned are time-integrals of energies divided by totals of the times, we may conveniently divide the whole class of problems, with reference to which the doctrine comes into question, into two classes.

Class I.: Those in which the velocities considered are either constant or only vary suddenly—that is to say, in infinitely small times—or in times so short that they may be omitted from the time-integration. To this class belong:

(a) The original Waterston-Maxwell case and the collisions of ideal rigid bodies of any shape, according to the assumed law that the translatory and rotatory motions lose no energy in the collisions.

(b) The frictionless motion of one or more particles constrained to remain on a surface of any shape, this surface being either closed (commonly called finite though really endless), or being a finite area of plane or curved surface, bounded like a billiard table, by a wall or walls, from which impinging particles are reflected at angles equal to the angles of incidence.

(c) A closed surface, with non-vibratory particles moving within it freely except during impacts of particles against one another or against the bounding surface.

(d) Cases such as (a), (b), or (c), with impacts against boundaries and mutual impacts between particles, softened by the supposition of finite forces during the impacts, with only the condition that the durations of the impacts are so short as to be practically negligible, in comparison with the durations of free paths.

Class II.: Cases in which the velocities of some of the particles concerned sometimes vary gradually; so gradually that the times during which they vary must be included in the time-integration. To this class belong examples such as (d) of Class I. with durations of impacts not negligible in the time-integration.

§ 29. Consider first Class I. (b) with a finite closed surface as the field of motion and a single particle moving on it. If a particle is given, moving in any direction through any point  $I$  of the field, it will go on for ever along one determinate geodetic line. The question that first occurs is, does the motion fulfil Maxwell's condition (see § 18 above); that is to say, for this case, if we go along the geodetic line long enough, shall we pass infinitely nearly to any point  $Q$  whatever, including  $I$ , of the surface an infinitely great number of times in all directions? This question cannot be answered in the affirmative without reservation. For example, if the surface be exactly an ellipsoid it must be answered in the negative, as is proved in the following §§ 30, 31, 32.

§ 30. Let  $A A'$ ,  $B B'$ ,  $C C'$ , be the ends of the greatest, mean, and least diameters of an ellipsoid. Let  $U_1$   $U_2$   $U_3$   $U_4$  be the umbilics in the arcs  $AC$ ,  $CA'$ ,  $A'C'$ ,  $C'A$ . A known theorem in the geometry of the ellipsoid tells us, that every geodetic through  $U_1$  passes through  $U_3$ , and every geodetic through  $U_2$  passes through

$U_4$ . This statement regarding geodetic lines on an ellipsoid of three unequal axes is illustrated by Fig. 1, a diagram showing for the extreme case in which the shortest axis is zero, the exact construction of a geodetic through  $U_1$  which is a focus of the ellipse shown in the diagram.  $U_3, C', U_4$  being infinitely near to  $U_1, C, U_2$  respectively are indicated by double letters at the same points. Starting from  $U_1$  draw the geodetic  $U_1 Q U_3$ ; the two parts of which  $U_1 Q$  and  $Q U_3$  are straight lines. It is interesting to remark that in whatever direction we start from  $U_1$  if we continue the geodetic through  $U_3$ , and on through  $U_1$  again and so on endlessly, as indicated in the diagram by the straight lines  $U_1 Q U_3 Q' U_1 Q'' U_3 Q'''$ , and so on, we come very quickly to lines approaching successively more and more nearly to coincidence with the major axis. At every point

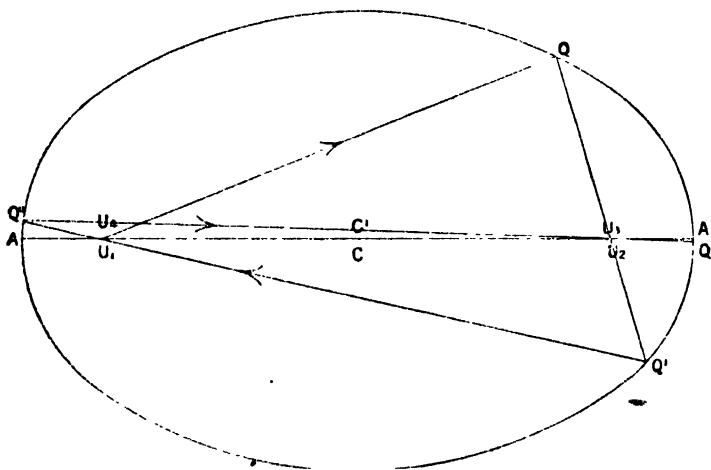


FIG. 1.

where the path strikes the ellipse it is reflected at equal angles to the tangent. The construction is most easily made by making the angle between the reflected path and a line to one focus, equal to the angle between the incident path and a line to the other focus.

§ 31. Returning now to the ellipsoid :—From any point  $I$ , between  $U_1$  and  $U_2$ , draw the geodetic  $I Q$ , and produce it through  $Q$  on the ellipsoidal surface. It must cut the arc  $A' C' A$  at some point between  $U_3$  and  $U_4$ , and, if continued on and on, it must cut the ellipse  $A O A' C' A$  successively between  $U_1$  and  $U_2$ , or between  $U_3$  and  $U_4$ ; never between  $U_2$  and  $U_3$ , or  $U_4$  and  $U_1$ . This, for the extreme case of the smallest axis zero, is illustrated by the path  $I Q Q' Q'' Q''' Q'''' Q'$  in Fig. 2.

§ 32. If now, on the other hand, we commence a geodetic through

any point  $J$  between  $U_1$  and  $U_4$ , or between  $U_2$  and  $U_3$ , it will never cut the principal section containing the umbilics, either between  $U_1$  and  $U_2$  or between  $U_3$  and  $U_4$ . This for the extreme case of  $C C' = 0$  is illustrated in Fig. 3.

§ 33. It seems not improbable that if the figure deviates by ever so little from being exactly ellipsoidal, Maxwell's condition might be fulfilled. It seems indeed quite probable that Maxwell's condition (see §§ 13, 29, above) is fulfilled by a geodetic on a closed surface of any shape in general, and that exceptional cases, in which the question of § 29 is to be answered in the negative, are merely particular surfaces of definite shapes, infinitesimal deviations from which will allow the question to be answered in the affirmative.

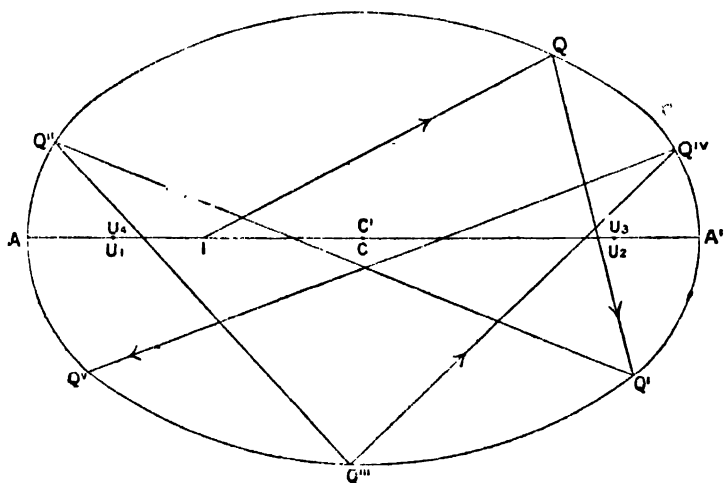


FIG. 2.

§ 34. Now with an affirmative answer to the question—is Maxwell's condition fulfilled?—what does the Boltzmann-Maxwell doctrine assert in respect to a geodetic on a closed surface? The mere wording of Maxwell's statement, quoted in § 13 above, is not applicable to this case, but the meaning of the doctrine as interpreted from previous writings both of Boltzmann and Maxwell, and subsequent writings of Boltzmann, and of Rayleigh,\* the most recent supporter of the doctrine, is that a single geodetic drawn long enough will not only fulfil Maxwell's condition of passing infinitely near to every point of the surface in all directions, but will pass with equal frequencies in all directions; and as many times within a certain infinitesimal distance  $\pm \delta$  of any one point  $P$  as of any other point  $P'$

\* Phil. Mag., January 1900.



the staple. [Boards of a considerable variety of shape with cords thus wound on them were shown as illustrations of the lecture.]

§ 36. A very easy way of drawing accurately the path of a particle moving in a plane and reflected from a bounding wall of any shape, provided only that it is not concave externally in any part, is furnished by a somewhat interesting kinematical method illustrated by the accompanying diagram (Fig. 4). It is easily realised by using two equal and similar pieces of board, cut to any desired figure, one of them being turned upside down relatively to the other, so that when the two are placed together with corresponding points in contact, each is the image of the other relative to the plane of contact regarded as a mirror. Sufficiently close corresponding points should be accurately marked on the boundaries of the two figures, and this allows great accuracy to be obtained in the drawing of the free path

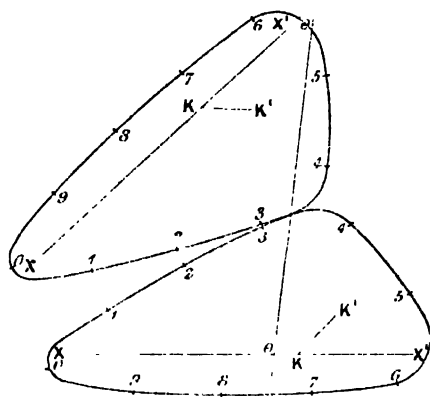


FIG. 4.

after each reflection. The diagram shows consecutive free paths 74.6—32.9 given, and 32.9—54.7, found by producing 74.6—32.9 through the point of contact. The process involves the exact measurement of the length ( $l$ )—say to three significant figures—and its inclination ( $\theta$ ) to a chosen line of reference  $XX'$ . The summations  $\sum l \cos 2\theta$  and  $\sum l \sin 2\theta$  give, as explained below, the difference of time integrals of kinetic energies of component motions parallel and perpendicular respectively to  $XX'$ , and parallel and perpendicular respectively to  $KK'$ , inclined at  $45^\circ$  to  $XX'$ . From these differences we find (by a procedure equivalent to that of finding the principal axes of an ellipse) two lines at right angles to one another, such that the time-integrals of the components of velocity parallel to them are respectively greater than and less than those of the components parallel to any other line. [This process was illustrated by models in the lecture.]

§ 37. Virtually the same process as this, applied to the case of a scalene triangle  $A B C$  (in which  $B C = 20$  centimetres and the angles  $A = 97^\circ$ ,  $B = 29^\circ.5$ ,  $C = 53^\circ.5$ ), was worked out in the Royal Institution during the fortnight after the lecture, by Mr. Anderson, with very interesting results. The length of each free path ( $l$ ), and its inclination to  $B C$  ( $\theta$ ), reckoned acute or obtuse according to the indications in the diagram, Fig. 5, were measured to the nearest millimetre and the nearest integral degree. The first free path was drawn at random, and the continuation, after 599 reflections (in all 600 paths), were drawn in a manner illustrated by Fig. 5, which shows, for example, a path  $P Q$  on one triangle continued to  $Q R$  on the other. The two when folded together round the line  $A B$  show a path  $P Q$ , continued on  $Q R$  after reflection. For each path  $l \cos 2\theta$  and  $l \sin 2\theta$  were calculated and entered in tables with the proper

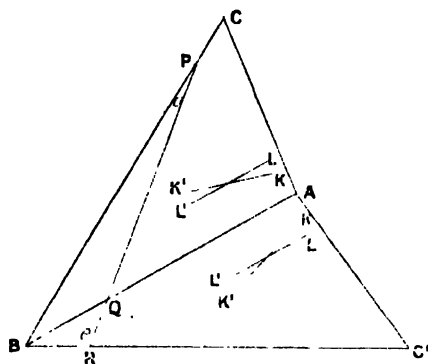


FIG. 5.

algebraic signs. Thus, for the whole 600 paths, the following summations were found :

$$\Sigma l = 3298; \quad \Sigma l \cos 2\theta = +128.8; \quad \Sigma l \sin 2\theta = -201.9.$$

Remark, now, if the mass of the moving particle is 2, and the velocity one centimetre per second,  $\Sigma l \cos 2\theta$  is the excess of the time-integral of kinetic energy of component motion parallel to  $B C$  above that of component motion perpendicular to  $B C$ , and  $\Sigma l \sin 2\theta$  is the excess of the time-integral of kinetic energy of component motion perpendicular to  $K K'$  above that of component motion parallel to  $K K'$ ;  $K K'$  being inclined at  $45^\circ$  to  $B C$  in the direction shown in the diagram. Hence the positive value of  $\Sigma l \cos 2\theta$  indicates a preponderance of kinetic energy due to component motion parallel to  $B C$  above that of component motion perpendicular to  $B C$ ; and the negative sign of  $\Sigma l \sin 2\theta$  shows preponderance of kinetic energy of component



motion parallel to  $KK'$ , above that of component motion perpendicular to  $KK'$ . Deducing a determination of two axes at right angles to each other, corresponding respectively to maximum and minimum kinetic energies, we find  $LL'$ , being inclined to  $KK'$  in the direction shown, at an angle  $= \frac{1}{2} \tan^{-1} \frac{128.8}{201.9}$ , is what we may call the axis of maximum energy, and a line perpendicular to  $LL'$  the axis of minimum energy; and the excess of the time-integral of the energy of component velocity parallel to  $LL'$  exceeds that of the component perpendicular to  $LL'$  by  $239.4$  being  $\sqrt{128.8^2 + 201.9^2}$ . This is

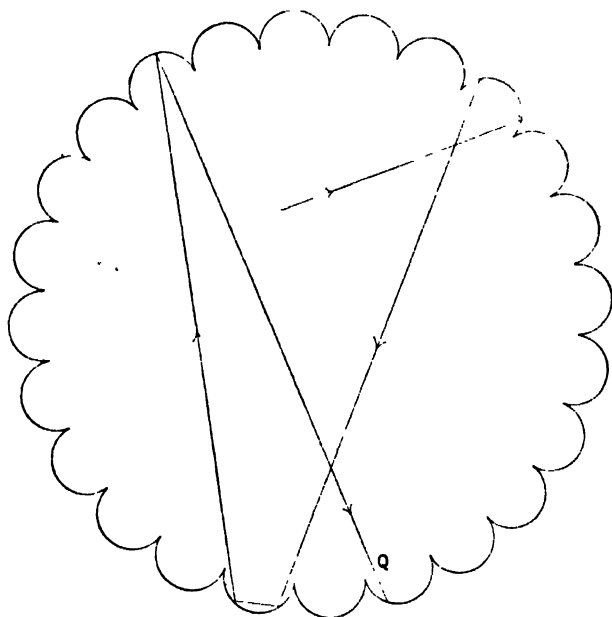


FIG. 6.

7.25 per cent. of the total of  $\Sigma l$  which is the time-integral of the total energy. Thus, in our result, we find a very notable deviation from the Boltzmann-Maxwell doctrine, which asserts for the present case that the time-integrals of the component kinetic energies are the same for all directions of the component. The percentage which we have found is not very large; and, most probably, summations for several successive 600 flights would present considerable differences, both of the amount of the deviation from equality and the direction of the axes of maximum and minimum energy. Still, I think there is a strong probability that the disproof of the Boltzmann-Maxwell doctrine

is genuine, and the discrepancy is somewhat approximately of the amount and direction indicated. I am supported in this view by scrutinising the thirty sums for successive sets of twenty flights: thus I find  $\sum l \cos 2\theta$  to be positive for eighteen out of thirty, and  $\sum l \sin 2\theta$  to be negative for nineteen out of the thirty.

§ 38. A very interesting test-case is represented in the accompanying diagram, Fig. 6—a circular boundary of semicircular corrugations. In this case it is obvious from the symmetry that the time-integral of kinetic energy of component motion parallel to any straight line must, in the long run, be equal to that parallel to any other. But the Boltzmann-Maxwell doctrine asserts, that the time-integrals of the kinetic energies of the two components, radial and transversal, according to polar co-ordinates, would be equal. To test this, I have taken the case of an infinite number of the semicircular corrugations, so that in the time-integral it is not necessary to include the times between successive impacts of the particle on any one of the semicircles. In this case the geometrical construction would, of course, fail to show the precise point Q at which the free path would cut the diameter AB of the semicircular hollow to which it is approaching; and I have evaded the difficulty in a manner thoroughly suitable for thermodynamic application such as the kinetic theory of gases. I arranged to draw lots for 1 out of the 199 points dividing AB into 200 equal parts. This was done by taking 100 cards,\* 0, 1 . . . . 98, 99, to represent distances from the middle point, and, by the toss of a coin, determining on which side of the middle point it was to be (plus or minus for head or tail, frequently changed to avoid possibility of error by bias). The draw for one of the hundred numbers (0 . . . . 99) was taken after very thorough shuffling of the cards in each case. The point of entry having been found, a large scale geometrical construction was used to determine the successive points of impact and the inclination  $\theta$  of the emergent path to the diameter AB. The inclination of the entering path to the diameter of the semicircular hollow struck at the end of the flight, has the same value  $\theta$ . If we call the diameter of the large circle unity, the length of each flight is  $\sin \theta$ . Hence, if the velocity is unity and the mass of the particle 2, the time-integral of the whole kinetic energy is  $\sin \theta$ ; and it is easy to prove that the time-integrals of the components of the velocity, along and perpendicular to the line from each point of the path to the centre of the large circle, are respectively  $\theta \cos \theta$ , and  $\sin \theta - \theta \cos \theta$ . The excess of the latter

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\* I had tried numbered billets (small squares of paper) drawn from a bowl, but found this very unsatisfactory. The best mixing we could make in the bowl seemed to be quite insufficient to secure equal chances for all the billets. Full sized cards like ordinary playing cards, well shuffled, seemed to give a very fairly equal chance to every card. Even with the full-sized cards, electric attraction sometimes intervenes and causes two of them to stick together. In using one's fingers to mix dry billets of card, or of paper, in a bowl, very considerable disturbance may be expected from electrification.

above the former is  $\sin \theta - 2 \theta \cos \theta$ . By summation for 143 flights we have found,

$$\Sigma \sin \theta = 121.3; 2 \Sigma \theta \cos \theta = 108.3;$$

whence,

$$\Sigma \sin \theta - 2 \Sigma \theta \cos \theta = 13.0.$$

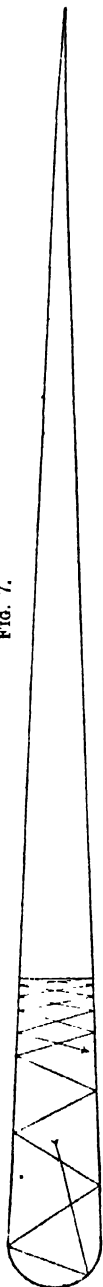
This is a notable deviation from the Boltzmann-Maxwell doctrine, which makes  $\Sigma (\sin \theta - \theta \cos \theta)$  equal to  $\Sigma \theta \cos \theta$ . We have found the former to exceed the latter by a difference which amounts to 10.7 of the whole  $\Sigma \sin \theta$ .

Out of fourteen sets of ten flights, I find that the time-integral of the transverse component is less than half the whole in twelve sets, and greater in only two. This seems to prove beyond doubt that the deviation from the Boltzmann-Maxwell doctrine is genuine; and that the time-integral of the transverse component is certainly smaller than the time-integral of the radial component.

§ 39. It is interesting to remark that our present result is applicable (see § 38 above) to the motion of a particle, flying about in an enclosed space, of the same shape as the surface of a marlin-spike (Fig. 7). Symmetry shows, that the axes of maximum or minimum kinetic energy must be in the direction of the middle line of the length of the figure and perpendicular to it. Our conclusion is that the time-integral of kinetic energy is maximum for the longitudinal component and minimum for the transverse. In the series of flights, corresponding to the 143 of Fig. 6, which we have investigated, the number of flights is of course many times 143 in Fig. 7, because of the reflections at the straight sides of the marlin-spike. It will be understood, of course, that we are considering merely motion in one plane through the axis of the marlin-spike.

§ 40. The most difficult and seriously troublesome statistical investigation in respect to the partition of energy which I have hitherto attempted, has been to find the proportions of translational and rotational energies in various cases, in each of which a rotator experiences multitudinous reflections at two fixed parallel planes between which it moves, or at one plane to which it is brought back by a constant force through its centre of inertia, or by a force varying directly as the distance from the plane. Two different rotators were considered, one of them consisting of two equal masses, fixed at the ends of a rigid massless rod, and each particle reflected on striking either of the planes; the other consisting of

Fig. 7.



two masses, 1 and 100, fixed at the ends of a rigid massless rod, the smaller mass passing freely across the plane without experiencing any force, while the greater is reflected every time it strikes. The second rotator may be described, in some respects more simply, as a hard massless ball having a mass = 1 fixed anywhere eccentrically within it, and another mass = 100 fixed at its centre. It may be called, for brevity, a biased ball.

§ 41. In every case of a rotator whose rotation is changed by an impact, a transcendental problem of pure kinematics essentially occurs to find the time and configuration of the first impact; and another such problem to find if there is a second impact, and, if so, to determine it. Chattering collisions of one, two, three, four, five or more impacts, are essentially liable to occur, even to the extreme case of an infinite number of impacts and a collision consisting virtually of a gradually varying finite pressure. Three is the greatest number of impacts we have found in any of our calculations. The first of these transcendental problems, occurring essentially in every case, consists in finding the smallest value of  $\theta$  which satisfies the equation

$$\theta - i = \frac{\omega a}{v} (1 - \sin \theta);$$

where  $\omega$  is the angular velocity of the rotator before collision;  $a$  is the length of a certain rotating arm;  $i$  its inclination to the reflecting plane at the instant when its centre of inertia crosses a plane  $F$ , parallel to the reflecting plane and distant  $a$  from it; and  $v$  is the velocity of the centre of inertia of the rotator. This equation is, in general, very easily solved by calculation (trial and error), but more quickly by an obvious kinematic method, the simplest form of which is a rolling circle carrying an arm of adjustable length. In our earliest work we performed the solution arithmetically, after that kinematically. If the distance between the two parallel planes is moderate in comparison with  $2a$  (the effective diameter of the rotator),  $i$  for the beginning of the collision with one plane has to be calculated from the end of the preceding collision against the other plane by a transcendental equation, on the same principle as that which we have just been considering. But I have supposed the distance between the two planes to be very great, practically infinite, in comparison with  $2a$ , and we have therefore found  $i$  by lottery for each collision, using 180 cards corresponding to  $180^\circ$  of angle. In the case of the biased globe, different equally probable values of  $i$  through a range of  $360^\circ$  was required, and we found them by drawing from the pack of 180 cards and tossing a coin for plus or minus.

§ 42. Summation for 110 flights of the rotator, consisting of two equal masses, gave as the time-integral of the whole energy, 200.03, and an excess of rotatory above translatory, 42.05. This is just 21 per cent. of the whole; a large deviation from the Boltzmann-

Maxwell doctrine, which makes the time-integrals of translatory and rotatory energies equal.

§ 43. In the solution for the biassed ball (masses 1 and 100), we found great irregularities due to "runs of luck" in the toss for plus or minus, especially when there was a succession of five or six pluses or five or six minuses. We therefore, after calculating a sequence of 200 flights with angles each determined by lottery, calculated a second sequence of 200 flights with the equally probable set of angles given by the same numbers with altered signs. The summation for the whole 400 gave  $555 \cdot 5$  as the time-integral of the whole energy, and an excess,  $82 \cdot 5$ , of the time-integral of the translatory, over the time-integral of the rotatory energy. This is nearly 15 per cent. We cannot, however, feel great confidence in this result, because the first set of 200 made the translatory energy less than the rotatory energy by a small percentage ( $2 \cdot 3$ ) of the whole, while the second 200 gave an excess of translatory over rotatory amounting to  $35 \cdot 9$  per cent. of the whole.

§ 44. All our examples considered in detail or worked out, hitherto, belong to Class I. of § 28. As a first example of Class II., consider a case merging into the geodetic line on a closed surface  $S$ . Instead of the point being constrained to remain on the surface, let it be under the influence of a field of force, such that it is attracted towards the surface with a finite force, if it is placed anywhere very near the surface on either side of it, so that if the particle be placed on  $S$  and projected perpendicularly to it, either inwards or outwards, it will be brought back before it goes further from the surface than a distance  $h$ , small in comparison with the shortest radius of curvature of any part of the surface. The Boltzmann-Maxwell doctrine asserts that the time-integral of kinetic energy of component motion normal to the surface, would be equal to half the kinetic energy of component motion at right angles to the normal; by normal being meant, a straight line drawn from the actual position of the point at any time perpendicular to the nearest part of the surface  $S$ . This, if true, would be a very remarkable proposition. If  $h$  is infinitely small, we have simply the mathematical condition of constraint to remain on the surface, and the path of the particle is exactly a geodetic line. If the force towards  $S$  is zero, when the distance on either side of  $S$  is  $\pm h$ , we have the case of a particle placed between two guiding surfaces with a very small distance,  $2h$ , between them. If  $S$ , and therefore each of the guiding surfaces, is in every normal section convex outwards, and if the particle is placed on the outer guide-surface, and projected in any direction in it, with any velocity, great or small, it will remain on that guide-surface for ever, and travel along a geodetic line. If now it be deflected very slightly from motion in that surface, so that it will strike against the inner guide-surface, we may be quite ready to learn, that the energy of knocking about between the two surfaces, will grow up from something very small in the beginning, till, in the long run, its time-integral is

comparable with the time-integral of the energy of component motion parallel to the tangent plane of either surface. But will its ultimate value be exactly half that of the tangential energy, as the doctrine tells us it would be? We are, however, now back to Class I.; we should have kept to Class II., by making the normal force on the particle always finite, however great.

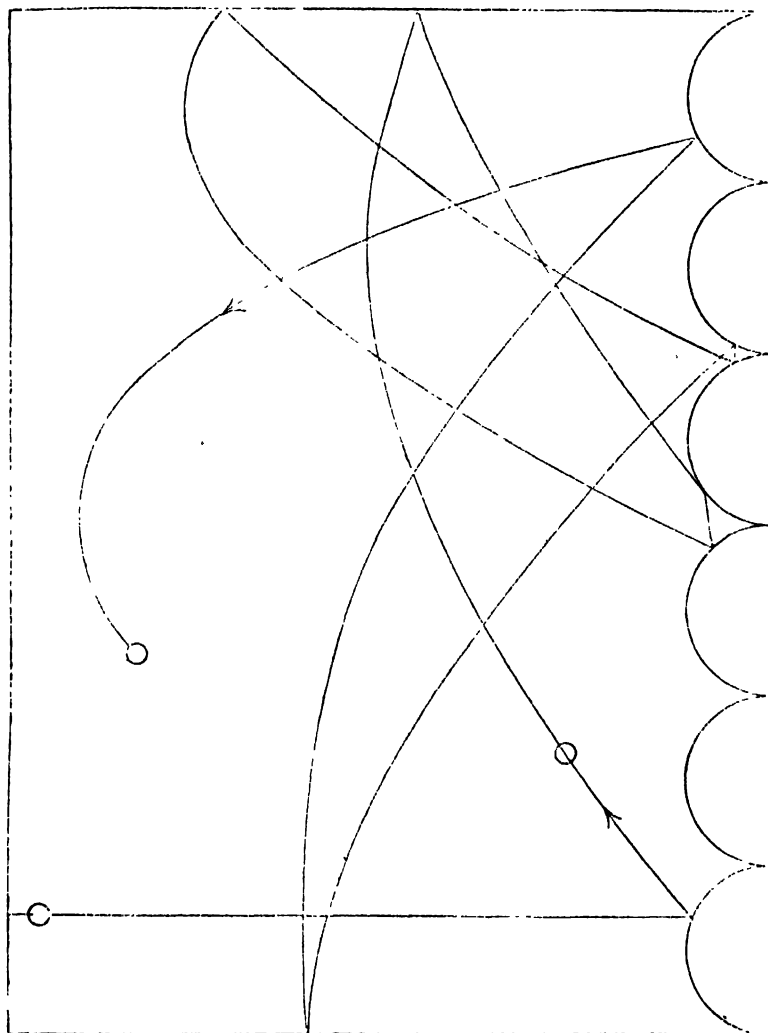
§ 45. Very interesting cases of Class II., § 28, occur to us readily in connection with the cases of Class I. worked out in §§ 38, 41, 42, 43.

§ 46. Let the radius of the large circle in § 38 become infinitely great: we have now a plane F (floor) with *semicircular cylindric hollows*, or semicircular hollows as we shall say for brevity; the motion being confined to one plane perpendicular to F, and to the edges of the hollows. For definiteness we shall take for F the plane of the edges of the hollows. Instead now of a particle after collision flying along the chord of the circle of § 38, it would go on for ever in a straight line. To bring it back to the plane F, let it be acted on either ( $\alpha$ ) by a force towards the plane in simple proportion to the distance, or ( $\beta$ ) by a constant force. This latter supposition ( $\beta$ ) presents to us the very interesting case of an elastic ball bouncing from a corrugated floor, and describing gravitational parabolas in its successive flights, the durations of the different flights being in simple proportion to the component of velocity perpendicular to the plane F. The supposition ( $\alpha$ ) is purely ideal; but, it is interesting because it gives a half curve of sines for each flight, and makes the times of flight from F after a collision and back again to F the same for all the flights, whatever be the inclination on leaving the floor and returning to it. The supposition ( $\beta$ ) is illustrated in Fig. 8, with only the variation that the corrugations are convex instead of concave, and that two vertical planes are fixed to reflect back the particle, instead of allowing it to travel indefinitely, either to right or to left.

§ 47. Let the rotator of §§ 41 to 43, instead of bouncing to and fro between two parallel planes, impinge only on one plane F, and let it be brought back by a force through its centre of inertia, either ( $\alpha$ ) varying in simple proportion to the distance of the centre of inertia from F, or ( $\beta$ ) constant. Here, as in § 46, the times of flight in case ( $\alpha$ ) are all the same, and in ( $\beta$ ) they are in simple proportion to the velocity of its centre of inertia when it leaves F or returns to it.

§ 48. In the cases of §§ 46, 47, we have to consider the time-integral for each flight of the kinetic energy of the component velocity of the particle perpendicular to F, and of the whole velocity of the centre of inertia of the rotator, which is itself perpendicular to F. If  $q$  denotes the velocity perpendicular to F of the particle, or of the centre of inertia of the rotator, at the instants of crossing F at the beginning and end of the flight, and if 2 denotes the mass of the particle or of the rotator so that the kinetic energy is the same as the square of the velocity, the time-integral is in case ( $\alpha$ )  $\frac{1}{2} q^2 T$  and in case ( $\beta$ )  $\frac{1}{2} q^2 T$ , the time of the flight being denoted in each case by T.

In both ( $\alpha$ ) and ( $\beta$ ), § 46, if we call 1 the velocity of the particle, which is always the same, we have  $q^2 = \sin^2 \theta$ , and the other component of the energy is  $\cos^2 \theta$ . In § 47 it is convenient to call



the total energy 1; and thus  $1 - q^2$  is the total rotational energy, which is constant throughout the flight. Hence, remembering that the times of flight are all the same in case ( $\alpha$ ) and are proportional

to the value of  $q$  in case ( $\beta$ ); in case ( $\alpha$ ), whether of § 46 or § 47, the time-integrals of the kinetic energies to be compared are as  $\frac{1}{2} \Sigma q^2$  to  $\Sigma (1 - q^2)$ , and in case ( $\beta$ ) they are as  $\frac{1}{2} \Sigma q^3$  and  $\Sigma q (1 - q^2)$ .

§ 49. Hence with the following notation—

$$\text{In § 46 } \begin{cases} \text{time-integral of kinetic energy perpendicular to } F, = V \\ \text{,, ,, parallel to } F, = U \end{cases}$$

$$\text{In § 47 } \begin{cases} \text{translatory energy} = V \\ \text{,, rotatory ,,} = R \end{cases}$$

we have

$$\frac{V - U}{V + U} \begin{cases} = \frac{\Sigma (\frac{3}{2} q^2 - 1)}{\Sigma (1 - \frac{1}{2} q^2)} & \text{in case } (\alpha) \\ = \frac{\Sigma (\frac{1}{2} q^3 - q)}{\Sigma (q - \frac{2}{3} q^3)} & \text{,, } (\beta) \end{cases}$$

$$\frac{V - R}{V + R} \begin{cases} = \frac{\Sigma (\frac{3}{2} q^2 - 1)}{\Sigma (1 - \frac{1}{2} q^2)} & \text{,, } (\alpha) \\ = \frac{\Sigma (\frac{1}{2} q^3 - q)}{\Sigma (q - \frac{2}{3} q^3)} & \text{,, } (\beta) \end{cases}$$

§ 49. By the processes described above,  $q$  was calculated for the single particle and corrugated floor (§ 46), and for the rotator of two equal masses each impinging on a fixed plane (§§ 41, 42), and for the biassed ball (central and eccentric masses 100 and 1 respectively, §§ 41, 43). Taking these values of  $q$ , summing  $q$ ,  $q^2$  and  $q^3$  for all the flights, and using the results in § 48, we find the following six results:

Single particle bounding from corrugated floor (semicircular hollows), 143 flights:—

$$\frac{V - U}{V + U} \begin{cases} = + \cdot 197 & \text{for isochronous sinusoidal flights.} \\ = + \cdot 136 & \text{for gravitational parabolic ,,} \end{cases}$$

Rotator of two equal masses, 110 flights:—

$$\frac{V - R}{V + R} \begin{cases} = - \cdot 179 & \text{for isochronous sinusoidal flights.} \\ = - \cdot 150 & \text{for gravitational parabolic ,,} \end{cases}$$

Biassed ball, 400 flights:—

$$\frac{V - R}{V + R} \begin{cases} = + \cdot 025 & \text{for isochronous sinusoidal flights.} \\ = - \cdot 014 & \text{for gravitational parabolic ,,} \end{cases}$$

The smallness of the deviation of the last two results from what the Boltzmann-Maxwell doctrine makes them, is very remarkable when we compare it with the 15 per cent. which we have found (§ 43 above) for the biassed ball bounding free from force, to and fro between two parallel planes.



§ 50. The last case of partition of energy which we have worked out statistically, relates to an impactual problem belonging partly to Class I., § 28, and partly to Class II. It was designed as a nearer approach to practical application in thermodynamics than any of those hitherto described. It is, in fact, a one-dimensional illustration of the kinetic theory of gases. Suppose a row of a vast number of atoms, of equal masses, to be allowed freedom to move only in a straight line between fixed bounding planes L and K. Let P the atom next K be caged between it and a parallel plane C, at a distance from it very small in comparison with the average of the free paths of the other particles; and let Q, the atom next to P, be perfectly free to cross the cage-front C, without experiencing force from it. Thus, while Q gets freely into the cage to strike P, P cannot follow it out beyond the cage-front. The atoms being all equal, every simple impact would produce merely an interchange of velocities between the colliding atoms, and no new velocity could be introduced, if the atoms were perfectly hard (§ 16 above), because this implies that no three can be in collision at the same time. I do not, however, limit the present investigation to perfectly hard atoms. But, to simplify our calculations, we shall suppose P and Q to be infinitely hard. All the other atoms we shall suppose to have the property defined in § 21 above. They may pass through one another in a simple collision, and go asunder each with its previous velocity unaltered, if the differential velocity be sufficiently great; they must recoil from one another with interchanged velocities if the initial differential velocity was not great enough to cause them to go through one another. Fresh velocities will generally be introduced, by three atoms being in collision at the same time, so that even if the velocities were all equal, to begin with, inequalities would supervene in virtue of three or more atoms being in collision at the same time; whether the initial differential velocities be small enough to result in two recoils, or whether one or both the mutual approaches lead to a passage or passages through one another. Whether the distribution of velocities, which must ultimately supervene, is or is not according to the Maxwellian law, we need not decide in our minds; but, as a first example, I have supposed the whole multitude to be given with velocities distributed among them according to that law (which, if they were infinitely hard, they would keep for ever after); and we shall further suppose equal average spacing in different parts of the row, so that we need not be troubled with the consideration of waves, as it were of sound, running to and fro along the row.

§ 51. For our present problem we require two lotteries, to find the influential conditions at each instant, when Q enters P's cage—lottery I. for the velocity ( $v$ ) of Q at impact; lottery II. for the phase of P's motion. For lottery I. (after trying 837 small squares of paper with velocities written on them and mixed in a bowl, and finding the plan unsatisfactory), we took nine stiff cards, numbered

1, 2 . . . 9, of the size of ordinary playing cards, with rounded corners, with one hundred numbers written on each in ten lines of ten numbers. The velocities on each card are shown on the following table. The number of times each velocity occurs was chosen to

fulfil as nearly as may be the Maxwellian law, which is  $C dv e^{-\frac{v^2}{k}}$  = the number of velocities between  $v + \frac{1}{2} dv$  and  $v - \frac{1}{2} dv$ . We took  $k = 1$ , which, if  $dv$  were infinitely small, would make the mean of the squares of the velocities equal exactly to  $\cdot 5$ ; we took  $dv = \cdot 1$  and  $C dv = 108$ , to give, as nearly as circumstances would allow, the

TABLE SHOWING THE NUMBER OF THE DIFFERENT VELOCITIES ON THE DIFFERENT CARDS.

Velocity.	·1	·2	·3	·4	·5	·6	·7	·8	·9	1·0	1·1	1·2	1·3	1·4	1·5	1·6	1·7	1·8	1·9	2·0	2·1	2·2	
Card 1	100																						
" 2		7	93																				
" 3			10	90																			
" 4				9	91																		
" 5					1	84	15																
" 6							60	40															
" 7								26	57	17													
" 8									31	40	29												
" 9											3	26	19	15	11	9	6	4	3	2	1	1	Σ v
Sums of velocities	107	103	99	92	84	75	66	57	48	40	32	26	19	15	11	9	6	4	3	2	1	1	900

Maxwellian law, and to make the total number of different velocities 900. The sum of the squares of all these 900 velocities is 468·4, which divided by 900 is  $\cdot 52$ . In the practice of this lottery, the numbered cards were well shuffled and then one was drawn; the particular one of the hundred velocities on this card to be chosen was found by drawing one card from a pack of one hundred numbered 1, 2 . . . 99, 100. In lottery II. a pack of one hundred cards is used to draw one of one hundred decimal numbers from  $\cdot 01$  to  $1\cdot 00$ . The decimal drawn, called  $\alpha$ , shows the proportion of the whole period of P from the cage-front C, to K, and back to C, still unperformed at the instant when Q crosses C. Now remark, that if Q overtakes P in the first half of its period, it gives its velocity,  $v$ , to P and follows it inwards; and therefore there must be a second impact when P meets it after reflection from K and gives it back the velocity  $v$  which it had on entering. If Q meets P in the second half of its period, Q

will, by the first impact, get P's original velocity, and may with this velocity escape from the cage. But it may be overtaken by P before it gets out of the cage, in which case it will go away from the cage with its own original velocity  $v$  unchanged. This occurs always if, and never unless,  $u$  is less than  $v$ ; P's velocity being denoted by  $u$ , and Q's by  $v$ . This case of Q overtaken by P can only occur if the entering velocity of Q is greater than the speed of P before collision. Except in this case, P's speed is unchanged by the collision. Hence we see, that it is only when P's speed is greater than Q's before collision, that there can be interchange, and this interchange leaves P with less speed than Q. If every collision involved interchange, the average velocity of P would be equalised by the collisions to the average velocity of Q, and the average distribution of different velocities would be identical for Q and P. Non-fulfilment of this equalising interchange can, as we have seen, only occur when Q's speed is less than P's, and therefore the average speed and the average kinetic energy of P must be less than the average kinetic energy of Q.

§ 52. We might be satisfied with this, as directly negating the Boltzmann-Maxwell doctrine for this case. It is, however, interesting to know, not only that the average kinetic energy of Q is greater than that of the caged atom, but, further, to know how much greater it is. We have therefore worked out summations for 300 collisions between P and Q, beginning with  $u^2 = .5$  ( $u = .71$ ), being approximately the mean of  $v^2$  as given by the lottery. It would have made no appreciable difference in the result if we had begun with any value of  $u$ , large or small, other than zero. Thus, for example, if we had taken 100 as the first value of  $u$ , this speed would have been taken by Q at the first impact, and sent away along the practically infinite row, never to be heard of again; and the next value of  $u$  would have been the first value drawn by lottery for  $v$ . Immediately before each of the subsequent impacts, the velocity of P is that which it had from Q by the preceding impact. In our work, the speeds which P actually had at the first sixteen times of Q's entering the cage were .71, .5, .3, .2, .2, .1, .1, .2, .2, .5, .7, .2, .3, .6, 1.5, .5—from which we see how little effect the choice of .71 for the first speed of P had on those that follow. The summations were taken in successive groups of ten; in every one of these  $\Sigma v^2$  exceeded  $\Sigma u^2$ . For the 300 we found  $\Sigma v^2 = 148.53$  and  $\Sigma u^2 = 61.62$ , of which the former is 2.41 times the latter. The two ought to be equal according to the Boltzmann-Maxwell doctrine. Dividing  $\Sigma v^2$  by 300 we find .495, which chances to more nearly the .5 we intended than the .52 which is on the cards (§ 51 above). A still greater deviation (2.71 instead of 2.41) was found by taking  $\Sigma v^3$  and  $\Sigma u^3$  to allow for greater probability of impact with greater than with smaller values of  $v$ ;  $u'$  being the velocity of P after collision with Q.

§ 53. We have seen in § 52 that  $\Sigma u^2$  must be less than  $\Sigma v^2$ , but it seemed interesting to find how much less it would be with

some other than the Maxwellian law of distribution of velocities. We therefore arranged cards for a lottery, with an arbitrarily chosen distribution, quite different from the Maxwellian. Eleven cards, each with one of the eleven numbers 1, 3 . . . 19, 21, to correspond to the different velocities  $\cdot 1, \cdot 3 \dots 1\cdot 9, 2\cdot 1$ , were prepared and used instead of the nine cards in the process described in § 51 above. In all except one of the eleven tens,  $\Sigma v^2$  was greater than  $\Sigma u^2$ , and for the whole 110 impacts we found  $\Sigma v^2 = 179\cdot 90$ , and  $\Sigma u^2 = 97\cdot 66$ ; the former of these is  $1\cdot 84$  times the latter. In this case we found the ratio of  $\Sigma v^3$  to  $\Sigma u^2 v$  to be  $1\cdot 87$ .

§ 54. In conclusion, I wish to refer, in connection with Class II. § 28, to a very interesting and important application of the doctrine, made by Maxwell himself, to the equilibrium of a tall column of gas under the influence of gravity. Take, first, our one-dimensional gas of § 50, consisting of a straight row of a vast number of equal and similar atoms. Let now the line of the row be vertical, and let the atoms be under the influence of terrestrial gravity, and suppose, first, the atoms to resist mutual approach, sufficiently to prevent any one from passing through another with the greatest relative velocity of approach that the total energy given to the assemblage can allow. The Boltzmann-Maxwell doctrine (§ 18 above) asserting as it does that the time integral of the kinetic energy is the same for all the atoms, makes the time-average of the kinetic energy the same for the highest as for the lowest in the row. This, if true, would be an exceedingly interesting theorem. But now, suppose two approaching atoms not to repel one another with infinite force at any distance between their centres, and suppose energy to be given to the multitude sufficient to cause frequent instances of two atoms passing through one another. Still the doctrine can assert nothing but that the time-integral of the kinetic energy of any one atom is equal to that of any other atom, which is now a self-evident proposition, because the atoms are of equal masses, and each one of them in turn will be in every position of the column, high or low. (If in the row there are atoms of different masses, the Waterston-Maxwell doctrine of equal average energies would, of course, be important and interesting.)

§ 55. But now, instead of our ideal one-dimensional gas, consider a real homogeneous gas, in an infinitely hard vertical tube, with an infinitely hard floor and roof, so that the gas is under no influence from without, except gravity. First, let there be only two or three atoms, each given with sufficient velocity to fly against gravity from floor to roof. They will strike one another occasionally, and they will strike the sides and floor and roof of the tube much more frequently than one another. The time-averages of their kinetic energies will be equal. So will they be if there are twenty atoms, or a thousand atoms, or a million, million, million, million, million atoms. Now each atom will strike another atom much more frequently than the sides or floor or roof of the tube. In the long run

each atom will be in every part of the tube as often as is every other atom. The time-integral of the kinetic energy of any one atom will be equal to the time-integral of the kinetic energy of any other atom. This truism is simply and solely all that the Boltzmann-Maxwell doctrine asserts for a vertical column of a homogeneous monatomic gas. It is, I believe, a general impression that the Boltzmann-Maxwell doctrine, asserting a law of partition of the kinetic part of the whole energy, includes obviously a theorem that the average kinetic energy of the atoms in the upper parts of a vertical column of gas, are equal to those of the atoms in the lower parts of the column. Indeed, with the wording of Maxwell's statement, § 18, before us, we might suppose it to assert that two parts of our vertical column of gas, if they contain the same number of atoms, must have the same kinetic energy, though they be situated, one of them near the bottom of the column, and the other near the top. Maxwell himself, in his 1866 paper ('The Dynamical Theory of Gases'),\* gave an independent synthetical demonstration of this proposition, and did not subsequently, so far as I know, regard it as immediately deducible from the partition doctrine generalised by Boltzmann and himself several years after the date of that paper.

§ 56. Both Boltzmann and Maxwell recognised the experimental contradiction of their doctrine presented by the kinetic theory of gases, and felt that an explanation of this incompatibility was imperatively called for. For instance, Maxwell, in a lecture on the dynamical evidence of the molecular constitution of bodies, given to the Chemical Society, Feb. 18, 1875, said: "I have put before you what I consider to be the greatest difficulty yet encountered by the molecular theory. Boltzmann has suggested that we are to look for the explanation in the mutual action between the molecules and the ethereal medium which surrounds them. I am afraid, however, that if we call in the help of this medium we shall only increase the calculated specific heat, which is already too great." Rayleigh, who has for the last twenty years been an unwavering supporter of the Boltzmann-Maxwell doctrine, concludes a paper 'On the Law of Partition of Energy,' published a year ago in the *Phil. Mag.*, Jan. 1900, with the following words: "The difficulties connected with the application of the law of equal partition of energy to actual gases have long been felt. In the case of argon and helium and mercury vapour, the ratio of specific heats (1.67) limits the degrees of freedoms of each molecule to the three required for translatory motion. The value (1.4) applicable to the principal diatomic gases, gives room for the three kinds of translation and for two kinds of rotation. Nothing is left for rotation round the line joining the atoms, nor for relative motion of the atoms in this line. Even if we regard the atoms as mere points, whose rotation means nothing, there must still exist

Addition, of date December 17, 1866. Collected works, vol. ii p. 76.

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"energy of the last-mentioned kind, and its amount (according to law) should not be inferior.

"We are here brought face to face with a fundamental difficulty, relating not to the theory of gases merely, but rather to general dynamics. In most questions of dynamics, a condition whose violation involves a large amount of potential energy may be treated as a constraint. It is on this principle that solids are regarded as rigid, strings as inextensible, and so on. And it is upon the recognition of such constraints that Lagrange's method is founded. But the law of equal partition disregards potential energy. However great may be the energy required to alter the distance of the two atoms in a diatomic molecule, practical rigidity is never secured, and the kinetic energy of the relative motion in the line of junction is the same as if the tie were of the feeblest. The two atoms, however related, remain two atoms, and the degrees of freedom remain six in number.

"What would appear to be wanted is some escape from the destructive simplicity of the general conclusion."

The simplest way of arriving at this desired result is to deny the conclusion; and so, in the beginning of the twentieth century, to lose sight of a cloud which has obscured the brilliance of the molecular theory of heat and light during the last quarter of the nineteenth century.

[K.]



Friday, January 18, 1901.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.  
President, in the Chair.

PROFESSOR DEWAR, M.A. LL.D. D.Sc. F.R.S. M.R.I.

*Gases at the Beginning and End of the Century.*

(Abstract.)<sup>1</sup>

It is interesting to review in broad outline the century's progress in some limited field of research. The subject of the Gases in its widest sense is too large a province to cover in a single discourse, but if the sketch is confined more especially to the growth of our knowledge of the change of state in gases, then the compass of the review becomes restricted to practicable dimensions.

At the beginning of the century the doctrines put forth in Lavoisier's 'Elements of Chemistry,' held overwhelming sway. The various states of matter were explained as arising from variations in the amount of caloric with which the body was penetrated. The term caloric must be interpreted as meaning the repulsive cause, whatever that may be, which separates the particles of matter from each other. According as the repulsive power is equal to, stronger, or weaker than, the attraction of the particles the substance became liquid, gaseous or solid. As a general principle it was assumed that every body in nature was susceptible of taking on solid, liquid or aeriform states.

The elastic aeriform fluids were now characterised for the first time under the generic term gases. A clear distinction was, however, drawn between the caloric which might be said to act like a solvent and the substance or base of the gas with which it was combined.

The particles of bodies, according to Lavoisier's view, do not make contact with each other, the intervals between them varying according to the figures and magnitude and the existing proportion between their inherent attraction and the repulsive force exerted in them by the caloric. The presentation of caloric, sometimes as a real material or very subtle fluid, did not prevent Lavoisier from generalising with profound sagacity on the fundamental similarity of all known gases. Thus, some thirty years before the definite liquefaction of any gas at that time regarded as permanent, in speculating on what would occur provided the earth were suddenly transported into a very cold region, he said, "In this case, the air, or at least some of the aeriform fluids which now compose the mass of our atmosphere,

would doubtless lose their elasticity for want of a sufficient temperature to retain them in that state; they would return to the fluid state of existence, and new liquids would be formed of whose properties we cannot at present form the most distant idea."

Dalton, in his paper 'On the force of steam or vapour from water and various other liquids both in a vacuum and in air,' published in 1802, arrived at the conclusion that, "there can scarcely be a doubt entertained respecting the reducibility of all elastic fluids of whatever kind into liquids; and we ought not to despair of effecting it in low temperature and by strong pressure exerted upon the unmixed gases." Here we notice Dalton introduces the novelty of suggesting the application of combining high pressure and low temperature on the pure gases, which led in 1823 to the successful experiments of Northmore, and then of Faraday and Davy. Thomas Young, in the lectures he delivered in this Institution early in the last century, and subsequently published, in 1807, under the title 'A Course of Lectures on Natural Philosophy and the Mechanical Arts,' after a careful analysis of all the existing experimental data, strongly supported the view that heat was a quality of the particles of bodies, and that that quality could only be motion. In explanation of the action of heat he says, "The effects of heat on the cohesive and repulsive powers of bodies have sometimes been referred to the centrifugal forces and mutual collisions of the revolving and vibrating particles; and the increase of the elasticity of aeriform fluids has been very minutely compared with the force which would be derived from an acceleration of these internal motions." (Young, 1807.) In the 'Elements of Chemical Philosophy,' published in 1812, Davy, in order to guard against the supposition that the doctrine of a specific fluid of heat was a necessary part of the principles of philosophical chemistry, threw out the following suggestions as the basis of a rational theory of the causes inducing change of state in matter; following the dictum, that the immediate cause of the phenomenon of heat is motion. Thus he says, "It seems possible to account for all the phenomena of heat if it be supposed that in solids the particles are in a constant state of vibratory motion, the particles of the hottest bodies moving with the greatest velocity and through the greatest space; that in fluids and elastic fluids, besides the vibratory motion, which must be conceived greatest in the last, the particles have a motion round their own axes with different velocities, the particles of elastic fluids moving with the greatest quickness; and that in ethereal substances the particles move round their own axes, and separate from each other, penetrating in right lines through space. Temperature may be conceived to depend upon the velocities of the vibrations; increase of capacity on the motion being performed in greater space, and the diminution of temperature during the conversion of solids into fluids or gases, may be explained on the idea of the loss of vibratory motion in consequence of the revolution of particles round their axes at the moment when the body becomes fluid or aeriform, or from loss of rapidity of vibration in consequence of the motion of the particles through greater

space." Later investigators, while altering the details of Davy's theoretical explanations of the gaseous state, in substance acknowledged the legitimacy of his ideas by extending and perfecting his hypothesis. A short time after the publication of Dalton's 'New System of Chemical Philosophy,' Leslie and Wollaston made their memorable experiments on the freezing of water by inducing rapid evaporation of the isolated liquid in a receiver by chemically absorbing or condensing the vapour as quickly as it is produced in a separate part of the same vessel. Thus originated the process of reaching lower temperatures and maintaining them by the continuous distillation of a fluid, or what is now called distillation *in vacuo* or under reduced pressure. Gay Lussac succeeded in showing that by such means a temperature as low as the freezing-point of mercury could be reached. Cagniard de la Tour in 1822 made his most startling experiments, proving that the dilatation of liquids has a limit beyond which, in spite of compression, they become gases. He succeeded in vaporising ether in a space twice the volume of the liquid, and noticed that before disappearing the liquid seemed to occupy the whole space; the tube finally looking empty, until on cooling a thick mist appeared for a minute, and then suddenly the liquid in the old state. This change in the case of ether from the liquid to the gas he showed took place at  $160^{\circ}$ , the pressure then being 37 to 38 atmospheres. He made similar experiments with alcohol, bisulphide of carbon and water, showing that the same state could be brought about in each case, only at different temperatures and pressures for each substance. This beautiful investigation, involving the use of sealed tubes together with manometric observations—the temperatures and pressure being very considerable—was indeed of first-rate importance, but its real value was not appreciated until many years later.

In the experiments of Faraday and Davy high pressures were obtained by generating the gases in sealed tubes bent into the shape of an inverted U, so that one leg containing the re-acting chemicals might be heated if necessary, and the other cooled to form a condenser for the liquefied gas. Davy, who was always alive to the possibility of practical utility resulting from scientific discovery, had the idea of using liquid gases as agents for the production of motive power and as the means by which great reductions of temperature could be effected, owing to the rapidity with which they could be rendered aeriform. Although Davy's mechanical suggestion has not been generally adopted, there can be no doubt about the successful application of such liquids to command steady low temperatures by their evaporation.

The next great advance was the production of large quantities of liquid carbonic acid by Thilorier in 1835, and the remarkable discovery that when ejected into the air its rapid evaporation reduced the temperature to such an extent as to cause its own solidification into the well-known snow. He further observed that the coefficient of expansion of the liquid gas is greater than that of any aeriform

body. No wonder that Thilorier should say that inside a Faraday tube was a new world in which totally unexpected phenomena occurred.

Faraday, by evaporating the carbonic acid snow in an exhausted receiver, succeeded in lowering the boiling point from  $-78^{\circ}$  C. to  $-110^{\circ}$  C. Combining the action of this low temperature with pressure, all gases by the year 1844 were liquefied, with the exception of the three elementary gases, hydrogen, nitrogen, oxygen, and the compound gases, carbonic oxide, marsh gas and nitric oxide. Andrews, some twenty-five years after the work of Faraday, attempted to induce change of state in the uncondensed gases, by using much higher pressures than Faraday employed. Combining the temperature of the solid carbonic acid bath with pressures of 300 atmospheres, Andrews found that none of the gases exhibited any appearance of liquefaction even in such high states of condensation; so far as change of volume by high compression went, Andrews confirmed the earlier work of Natterer, showing that the gases become less and less compressible with growing pressure. While such investigations were proceeding, Regnault and Magnus had made refined observations on the laws of Boyle and Gay Lussac, but none had made a complete study of the isothermals of a liquefiable gas through wide ranges of temperature. This was accomplished by Andrews in 1869, and his Bakerian Lecture 'On the Continuity of the Gaseous and Liquid States of Matter' will always be regarded as an epoch-making investigation.

During the course of this research Andrews observed that liquid carbonic acid raised to a temperature of  $31^{\circ}$  C. lost the sharp concave surface of demarcation between the liquid and the gas, the space being now occupied by a homogeneous fluid which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ, due to great local alterations of density.

At temperatures above  $31^{\circ}$  C. the separation into two distinct kinds of matter could not be effected even when the pressure reached 400 atmospheres.

This limiting temperature of the change of state from gas to liquid Andrews called the critical temperature. He showed that this temperature is constant, and differs with each substance, and that it is always associated with a definite pressure peculiar to each body. Thus the two constants, the critical temperature and pressure, which have been of the greatest importance in subsequent investigation, came to be defined, and a complete experimental proof was given that "the gaseous and liquid states are only distinct stages of the same condition of matter, and are capable of passing into one another by a process of continuous change."

The fundamental idea that gaseous pressure was the result of a succession of strokes of bombarding particles was first put forward by Bernouilli about the middle of the eighteenth century. Later the same suggestion was employed by Lessage, of Geneva; and Herepath,

in his 'Mathematical Physics,' published in 1847, made a considerable advance in the application of the theory. Joule made a great step in 1821 by calculating the mean translational velocity of the particles of hydrogen required to produce in a closed space the pressure of one atmosphere at the melting point of ice; but the great advance in the application of the theory was due to Clausius, ably supported later on by Maxwell, Boltzmann, Meyer and Van der Waals.

A very important series of experiments was made by Joule and Kelvin 'On the Thermal Effects of Fluids in Motion,' about 1862, in which the thermometrical effects of passing gases through porous plugs furnished important data for the study of the mutual action of the gas molecules.

Such experiments, along with a knowledge of the specific and latent heat, together with the rate of diffusion, viscosity and thermal conductivity, furnished material for a complete thermo-dynamical treatment of the gaseous state. Professor Van der Waals entered upon this difficult inquiry in 1873 by publishing an essay 'On the Continuity of the Gaseous and Liquid States,' full of new and suggestive ideas.

The equation of continuity Van der Waals developed involved the use of three constants instead of one, as in the old law of Boyle and Charles, the latter being only utilised to express the relation of temperature, pressure and volume when the gas is far removed from its point of liquefaction. Of the two new constants, one represents the molecular pressure arising from the attraction between the molecules, the other four times the volume of the molecules.

Given these constants for a gas, Van der Waals showed that his equation not only fitted into the general characters of the isothermals, but also gave the values of the critical temperature, the critical pressure and the critical volume. In the case of carbonic acid the theoretical results were found to be in remarkable agreement with the experimental values of Andrews. This gave chemists the means of ascertaining the critical constants, provided sufficiently accurate data derived from the study of a few properly distributed isothermals of the gaseous substance were available. Such important data came into the possession of chemists when Amagat published his important paper on the isothermals of oxygen, nitrogen, hydrogen, ethylene, etc., in the year 1880. It now became possible to calculate the critical data with comparative accuracy for the gases oxygen and nitrogen. This was done by Sarrau in 1882, and the subsequent static liquefaction of oxygen by Wroblewski in 1883 confirmed the theoretical conclusions. No doubt a great impulse had been given to research in this department by the suggestive experiments of Pictet and Cailletet in 1878.

The theory of Van der Waals has been of the greatest importance in directing experimental investigation in attacking the difficult problem of the liquefaction of the permanent gases. In the space of an hour's lecture it is impossible to do justice to all the workers who have contributed materially to the advance of this department.

The following table of the names of investigators who have contributed to the experimental, theoretical, or practical study of gases at once suggests much deserving work that otherwise ought to have been discussed had time permitted. All we can do is to make in rapid succession the fundamental experiments illustrative of the great advances made during the century. [Experiments here.]

*Table of Investigators.*

Dalton, Gay Lussac, Faraday, Davy, Avogadro, Caignard de la Tour, Regnault, Magnus, Thilorier, Natterer, Deville, Graham, Joule, Kelvin, Andrews, Herepath, Wollaston, Clausius, Rankine, Maxwell, Boltzmann, Stoney, Tait, Van der Waals, Mendeleeff, Amagat, Rayleigh, Crookes, Pictet, Cailletet, Wroblewski, Olszewski, Kundt, Warburg, Witkowski, Onnes, Young, Ramsay, Leduc, Mathias, Siemens, Kirk, Coleman, Linde, etc. etc.

It is unnecessary to enter into any detailed discussion of the progress made since liquid air came to be an instrument of scientific research, as this has been done in previous Friday Evening Discourses; but recent improvements in apparatus and methods of manipulation may be worthy of consideration. The facility and ease of handling, storing and working with liquid gases is dependent on the use of vacuum vessels, many types of which may be seen in Diagram 1.

Fig. 8 of the diagram is a copy of the highly exhausted calorimeter used in 1875 in a research 'On the Physical Constants of Hydrogenium,'\* and which for all intents and purposes was a vacuum vessel made of brass instead of glass. The use of such an arrangement to guard against gain or loss of heat was a natural deduction from the early work of Dulong and Petit on Radiation. Many convenient forms may be given to such vessels, and several varieties are represented in the diagram. The types 3 and 9, containing a spiral-tube arrangement to relieve the contraction when the inner vessel has to be joined to the outer by a tube, are of special importance when regenerative methods have to be employed, because, while isolating the metallic coil, it allows the liquid gas as it is formed to drain away from the interior, and be collected in another vacuum vessel outside of the main apparatus. This device, developed after many unsuccessful attempts to construct such a vacuum vessel, was found to be essential for the easy production and collection of liquid hydrogen, and as all the Royal Institution designs for such special vessels have been made in Germany, they have been supplied to and utilised by other workers, unconscious, it may be, where or how they originated. Such vessels may be silvered in whole or in part, or the vacuum may be nothing but mercury vapour. When liquid hydrogen has to be kept naturally, the vacuum vessel in which it is collected is placed in another vessel full of liquid air, so that the external wall of the hydrogen vacuum vessel is kept at about  $-190^{\circ}\text{C.}$

\* Trans. Royal Society of Edin. vol. xxvii.

or better at a lower temperature by exhausting the surrounding air. Many combinations of vacuum vessels can be arranged, and the lower the temperature at which we have to operate the more useful they become.

As the great object in producing liquid gases is in the first place scientific utility in opening up new fields of research, the application of liquid hydrogen as an agent by means of which the more volatile gases contained in atmospheric air may be separated is of some interest.

The diagram, Fig. 1, will make the process of separation intelligible. *A* represents a vacuum-jacketed vessel, partly filled with liquid air, in which a second vessel *B*, was immersed. From the bottom of *B* a tube, *a*, passed up through the rubber cork which closed *A*, and from the top of *B* a second tube, *b*, passed through the cork and on to the rest of the apparatus. Each of these tubes had a stopcock, *m* and *n*, and the end of the tube *a* was open to the air. A wider tube also passed through the cork of *A* and led to an air-pump, whereby the pressure above the liquid air in *A* was reduced, and consequently the temperature of the liquid by resultant evaporation. To keep the inner vessel, *B*, covered with liquid, a fourth tube, *r*, passed through the cork, and its lower end, furnished with a valve, *p*, which could be opened and closed by the handle *q*, dipped into liquid air contained in the vessel *C*. As the pressure above the liquid in *A* was less than that of the atmosphere, on opening the valve *p* some of the liquid air was forced through *r* into *A* by the pressure of the atmosphere, and in this way the level of liquid in *A* was maintained at the required height.

Since *B* was maintained at the temperature of liquid air boiling at reduced pressure, the air it contained condensed on its sides, and when the stopcock *n* was closed and *m* opened more air passed in through the open end of *a*, and was in turn condensed. In this way *B* could be filled completely with liquid air, the whole of the most volatile gases being retained in solution in the liquid.

The tube *b*, passing from the top of *B*, was connected with a three-way stopcock *d*, by which it could be put in communication with the closed vessel *D*, or with the tube *e*, and by which also *D* and *e* could be connected. The tube *e* passed down nearly to the bottom of the vacuum-jacketed vessel *E*, and out again through the cork; and so on to a gauge *f*, and through a sparking tube *g* to a mercury pump *F*.<sup>\*</sup> The stopcock *n* being still closed, the whole of the apparatus between *n* and the pump, including the vessel *D*, was exhausted, and liquid hydrogen introduced into *E*. The three-way cock *d* was then turned so as to connect *b* with *D*, and close *e*, and then *n* opened. *B* was thereby put in communication with *D*, which was at a still lower temperature than *B*, the air being at 63° absolute, while the hydrogen is at 21° absolute, and any gas dissolved in the liquid air in *B*, along with some of the more volatile nitrogen, distilled

\* The Sprengel in figure is simply diagrammatic.

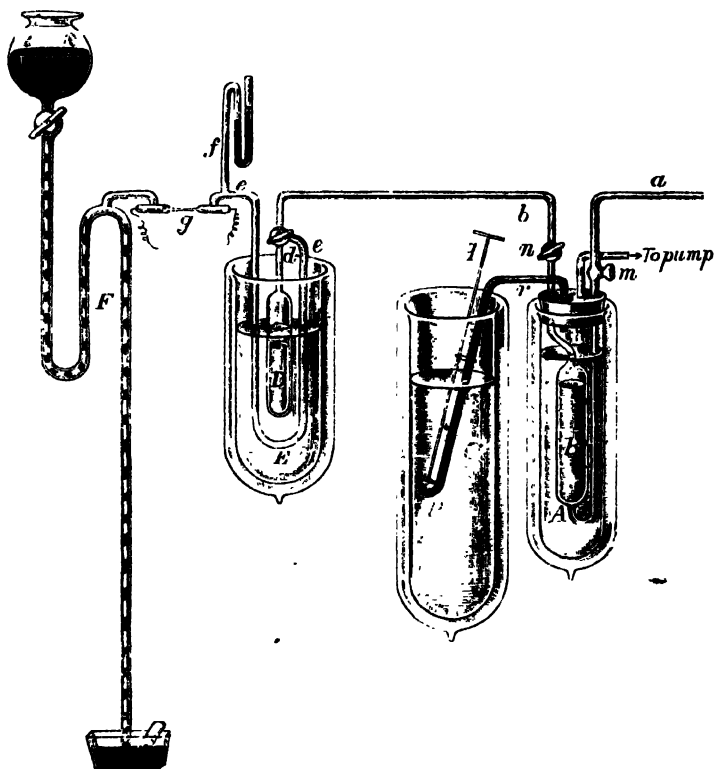


FIG. 1.



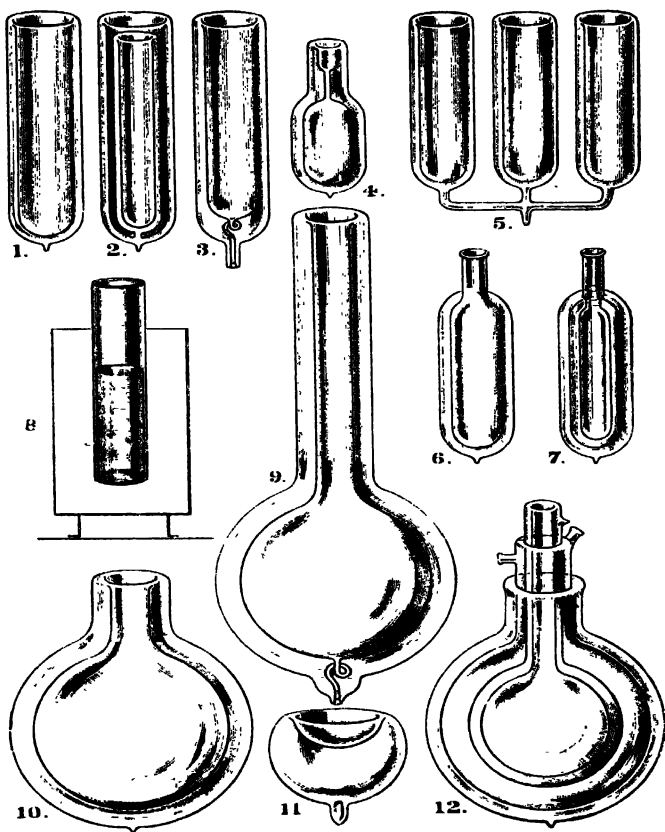


FIG. 2.

over, and the latter condensed in a solid form in *D*, while any gas incondensable at the boiling point of hydrogen filled the vessel at a low pressure, the latter being recorded by the manometer *f*. When a small fraction of the liquid in *B* had thus distilled, the stopcock *d* was turned so as to close the communication between *D* and *b* and open that between *D* and *e*. Gas from *D* passed into the sparking tube *g*, but in so doing it had to pass through the portion of *e* which was immersed in liquid hydrogen, so that condensable matter, like nitrogen or oxygen vapour, carried forward by the stream of gas, was frozen out.

On passing electric discharges through the tubes containing the most volatile of the atmospheric gases collected as above, they glow with a bright orange light, not only in the capillary part, but also at the poles, and at the negative pole in particular. The spectro-scope shows that this light consists in the visible part of the spectrum chiefly of a succession of strong rays in the red, orange, and yellow, attributed to hydrogen, helium, and neon. Besides these, a vast number of rays, generally less brilliant, are distributed through the whole length of the visible spectrum. They are obscured in the spectrum of the capillary part of the tube by the greater strength of the second spectrum of hydrogen, but are easily seen in the spectrum of the negative pole, which does not include the second spectrum of hydrogen, or only faint traces of it. Putting a Leyden jar in the circuit, while it more or less completely obliterates the second spectrum of hydrogen, it also has a similar effect on the greater part of these other rays of, as yet, unknown origin. The violet and ultra-violet part of the spectrum seems to rival in strength that of the red and yellow rays, if we may judge of it by the intensity of its impressions on photographic plates.

As these gases probably include some of the gases that pervade interplanetary space, search was made for the prominent nebular, coronal and auroral lines. No definite lines agreeing with the nebular spectrum could be found, but many lines occurred closely coincident with the coronal and auroral spectrum. Before any final conclusion can be reached, larger quantities of the gases must be collected, but this will not be difficult now that the method of separation has proved a success. It may safely be predicted that liquid hydrogen will be the means by which many obscure problems of physics and chemistry will ultimately be solved, so that the liquefaction of the last of the old permanent gases is as pregnant now with future consequences of great scientific moment as was the discovery of the liquefaction of chlorine in the early years of the century.

Friday, February 15, 1901.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

THE RIGHT REV. MONSIGNOR GERALD MOLLOY, D.D. D.Sc.

*Electric Waves.*

DR. MOLLOY said he had chosen the subject of electric waves, because he thought it represented one of the most important scientific developments of the closing years of the nineteenth century. He proposed, as far as might be within the limits of an hour, to give some general conception of the nature of these waves, to sketch very briefly the history of their discovery, and to show by a few simple experiments how their existence might be demonstrated, and their properties investigated.

He began by calling attention to the essential characteristics of wave motion, which he illustrated by a reference to waves of water, waves of sound, waves of light and radiant heat. He then said that the main purpose of his lecture was to bring home to them that electrical energy was transmitted through space by a motion of this kind; and that the medium through which this motion was conveyed was the ether, the same medium that served for the transmission of light and radiant heat.

Electric waves are most conveniently produced by a spark discharge. It was shown long ago by Professor William Thomson, now Lord Kelvin, that such a discharge, under certain conditions, was an oscillating phenomenon; that is, that the electric charge swings to and fro, like a pendulum, several times before it comes to rest. Each such oscillation would presumably involve some disturbance of the ether; these disturbances would be transmitted outwards and away in all directions; and following one another at regular intervals through space, would constitute a series of electric waves.

These ideas, which had been present, more or less vaguely, to the minds of scientific men for some time, were put into the form of a definite theory, supported by mathematical reasoning, by Professor Clerk Maxwell, about the year 1864. According to this theory, electrical energy is transmitted through space by vibrations or waves of ether; these vibrations travel with the same velocity as light; they are, in fact, vibrations of the same kind as light, differing only in the matter of wave-length; and if we could but increase the rate of vibration, thereby diminishing the wave-length, they would be-

come at first rays of dark heat, like those emitted by a hot metal plate, and then rays of light.

The truth of Maxwell's theory was experimentally demonstrated by Professor Heinrich Hertz, of Germany, in the year 1888, by a series of researches almost unrivalled for their brilliancy and thoroughness. His experiments, however, were only suitable to the laboratory, and various modifications were necessary in order to present the results in a sensible form before an audience.

The apparatus he had provided for this purpose might be said briefly to consist of two parts. At one end of the table was an arrangement intended to produce the electric waves. It consisted of an induction coil, and a pair of discharging rods ending in two brass knobs. This part he would call the oscillator. At the other end of the table was an arrangement intended to detect and reveal the presence of the electric waves. This part, which he called the resonator, was somewhat more complicated. First, there was a little piece of apparatus called the coherer. The coherer, as they knew, was a glass tube holding some metallic filings, which in their normal condition were practically a non-conductor of electricity, but which, when struck by electric waves, became a fairly good conductor. It was here mounted in the circuit of a small battery and an electric bell. In its normal condition, it opposed the passing of the current, and the bell was silent; when the electric waves arrived, it became a conductor—the current passed and the bell was rung. Thus the ringing of the bell would be a signal that the waves were there. A gentle tap on the coherer would restore it to its former condition, and it would be ready for a new experiment.

The lecturer now produced a spark in the oscillator, and the bell at once began to ring, proving that the electric waves had gone out from the oscillator and travelled through space to the resonator. A tap on the coherer reduced the bell to silence; and an assistant now proceeded to carry the resonator to various parts of the theatre. In every position it responded instantaneously to the spark of the oscillator; thus showing that electric waves, like waves of light and radiant heat, go out in all directions from the source of disturbance.

In the next experiment, the lecturer used two parabolic brass reflectors, which had been made many years ago for experiments on radiant heat. In the focus of one, he mounted a very small oscillator, which produced waves of some six or eight inches wave-length; while in the focus of the other he mounted a coherer in circuit with a small battery and bell. He then repeated with the electric waves produced in the oscillator, the well known experiment of the conjugate mirrors, and thus proved that the electric waves are subject to the same laws of reflection as waves of radiant heat and light.

With the same apparatus, he now tested the transparency and opacity of various bodies to electric waves—plate glass, sheet iron, indiarubber, wood. In particular, he called attention to the curious behaviour of plate glass with respect to waves of ether: it is very

transparent to electric waves; it is almost quite opaque to the much shorter waves of dark heat; it is again transparent to the still shorter waves of visible light; and it is again opaque to the shorter ultra-violet rays, and intensely opaque to the shortest waves of all, the X-rays.

The phenomenon of polarisation was next considered. From the way in which the waves are produced, we should expect to find that they are polarised at their source. It was shown how this might be tested by means of a frame over which a series of parallel copper wires were stretched. If the frame were held in the path of the waves, with the wires parallel to the spark, the grid would be opaque; if it were held with the wires perpendicular to the spark, the grid would be transparent. The experiment was tried, and the result fell out as expected. The grid behaved with respect to the electric waves, just as the analyser in a polariscope behaves with respect to a beam of plane polarised light.

The lecturer then called attention to the great variety of ether waves with which we are now acquainted, and having pointed out the position which each group occupies in the scale, said in conclusion: "Thus we come to realise that the various forms of energy to which, in common language, we give the names of electricity, magnetism, heat, light, chemical action, are all transmitted through space in the form of waves or vibrations of the ether; and that these vibrations are all essentially of the same kind, being distinguished from one another only by their wave-length. They produce widely different effects, when they strike upon our different senses; but considered in themselves they are only, so to say, notes of different pitch in the great scale of radiant energy which I have imperfectly attempted to sketch. This large and comprehensive view of radiant energy is one of the most notable results achieved by the great scientific men of the century that has just passed away. And the work that remains to be done by the coming generation, the great scientific men of the twentieth century, is to explore more thoroughly the properties of these ethereal waves, to fill up the gaps that still exist in the scale, and perhaps to reveal to the world the intrinsic constitution of the ether itself, that mystery of mysteries which underlies all those outward phenomena of nature."

Friday, March 22, 1901.

SIR JAMES CRIGHTON-BROWNE, M.D. LL.D. F.R.S., Treasurer and  
Vice-President, in the Chair.

HORACE T. BROWN, Esq., LL.D. F.R.S. M.B.I.

*Some Recent Work on Diffusion.*

THE subject of my lecture, though essentially of a physical nature, had its origin in what may be regarded as a no-man's land—a strip of neutral territory which can be claimed exclusively neither by the physicists nor the biologists.

An attempt to reconcile some apparently contradictory facts connected with the nutrition of plants has led, somewhat unexpectedly, to an extension of the laws of gaseous diffusion, so that we shall have to deal with one of those comparatively rare cases in which biology has been able to react to some extent on physics.

It has long been known that the primary source of the carbon of all plants is the carbonic acid existing in small quantities in ordinary atmospheric air, and that their green parts, more especially the leaves, are able to utilise the energy of sunlight in decomposing the carbonic acid and water, and building up from their elements a whole series of substances, such as sugars and starch, which contribute directly to the nutrition of the plant.

The immediate seat of this synthetic and assimilatory process is found in the minute green chlorophyll granules, which occur in great numbers within the cells of the leaf-tissue; and one of the first problems to be dealt with in the study of the process is to show in what manner the highly dilute carbonic acid of the air can gain entry into the leaf with sufficient rapidity to supply these assimilating centres with material for the needs of the plant.

In a typical leaf, such as is represented in section in the diagram, both sides are covered with a cuticle and epidermis, pierced at regular intervals on one or both sides with extremely minute openings, whose size is capable of being regulated according to the requirements of the plant. These are the *stomates*, which open out into a relatively large cavity within the leaf, and this cavity in turn communicates with the numerous and roomy air-spaces between the cells containing the green chlorophyll granules.

One of the most important functions of the stomates is undoubtedly to regulate the transpiration of water from the plant, but

the question of how far these minute openings play a part in the interchanges of gases between the interior of the leaf and the outer air, has been a subject of very lively controversy.

It is now about thirty years since the eminent French chemist, Boussingault, came to the conclusion that the carbonic acid of the air gains access to the leaf, not through the *stomates*, but through the continuous substance of the cuticle and epidermis, by a process of *osmosis* similar to that by which carbonic acid had been shown by Graham to pass through a thin film of india-rubber.

So convincing did Boussingault's experiments and arguments appear to his contemporaries that this view became an article of faith for something like a quarter of a century, until in fact, some five or six years ago, when Mr. F. Frost Blackman took up the subject and proceeded most inconsiderately to shatter all the most cherished statements of our text-books on this question.

I regret that time will not allow me to do more than state the general conclusions at which Mr. Blackman arrived, and which may be briefly summarised as follows :—

In the first place there is no appreciable passage of atmospheric carbonic acid through the surface of a leaf which is naturally devoid of stomates, such for instance as the upper surface of a normal leaf, which is quite imperforate; neither is any entry of carbonic acid possible when the stomates have been artificially blocked, or made to close spontaneously.

In addition to this, if a leaf has stomates on both surfaces, the intake of carbonic acid by those surfaces bears a distinct relation to the distribution of the stomates.

We can, in fact, no longer doubt that when a leaf is respiring or assimilating, mere osmosis of carbonic acid through the substance of the cuticle and epidermis plays little or no part in the gaseous exchanges, and that, whatever the exact nature of the process may be, it must be carried on exclusively by the minute openings of the stomates.

Since anything like a mass movement of the air through these openings is out of the question, we must look to the phenomena of *diffusion* for the true explanation, and especially to that form of it which was first described by Graham as *free diffusion*, that is to say, the natural tendency possessed by gases or liquids to form a perfect mixture when they are in contact with each other and there is no partition of any kind between them.

This spontaneous mixing is quite independent of any currents or mass movements of any kind, and is brought about by the gradual interpenetration of the molecules of the one gas or liquid by the molecules of the other.

As an example of this kind of diffusion, I have here a cylinder which, a few weeks ago, was partly filled with a 5 per cent. gelatine solution. After the gelatine had set, the cylinder was filled up with a highly coloured solution of copper salt, which you now see has permeated the jelly to a certain depth. There has been no mixing

of the solutions in the ordinary sense of the word, for the gelatine is virtually a solid. The effect has been produced by the molecules of the coloured copper salt, by reason of their rapid movement in all directions, gradually penetrating into the spaces between the molecules of the gelatine layer. Given a sufficient length of time, and there would be an equal partition of the coloured substance between the two layers.

Diffusion takes place, as is well known, much more rapidly with gases than with liquids. Had our cylinder contained, for instance, carbonic acid in the lower half and air in the upper, a complete mixing would have taken place in a comparatively short time, even if all convection currents had been prevented.

The classical researches of Graham on the diffusion of gases through thin porous septa established the general law that the rate of diffusion of the different gases, under identical conditions, varies inversely as the square roots of their respective densities. Graham's results, however, only acquaint us with the *relative* velocities of diffusion, whereas for the particular problem which we have before us, we must know the *absolute* velocities of diffusion under strictly defined conditions.

It is mainly to the Viennese school of physicists, and especially to Professor Loschmidt, that we owe our present knowledge of the actual rate of penetration of one gas by another in free diffusion.

By observing the speed with which different pairs of gases spontaneously mix in a tube, Loschmidt was able to deduce certain *absolute values* expressing the velocity of their interpenetration.

Some of these results for different pairs of gases are given in the diagram, the last column representing the "constant of diffusivity," expressed in centimetre-gram-second units.

Let us consider the constant for carbonic acid and air, which at  $0^{\circ}\text{C.}$  is  $\cdot 142$ . This means that when air and carbonic acid gas are freely diffusing into each other at this temperature, an amount of either gas corresponding to  $\cdot 142$  cubic centimetre will pass in one second of time, across an area of one square centimetre, when the partial pressure of the gas varies by one atmosphere in one centimetre of length.

Now when we come to apply these absolute values of diffusivity to the passage of the extremely dilute  $\text{CO}_2$  of the air into the leaf stomates (whose dimensions can of course be determined), we find that free diffusion through these openings is apparently able to account for only a portion of the gas which we know must enter the leaf, unless we make some extremely improbable assumptions as to the very low point at which the partial pressure of the carbonic acid is maintained immediately under the apertures.

I shall not, however, trouble you with the calculations on which this statement is based, since I prefer to put the matter in a more concrete form, which has also the advantage of emphasising the extraordinary power which an assimilating leaf possesses of extracting carbonic acid from its surrounding air.



There are two methods by which we can determine the actual amount of atmospheric carbonic acid used up by an assimilating leaf—one a direct, the other an indirect method.

Part of the apparatus used in the direct method, is shown on the table.

The leaf, which may be still attached to the plant, is enclosed in a glazed case through which a measured current of air is drawn, of which the carbonic acid content is accurately known. When the air emerges from the case it passes through an absorption apparatus which retains the whole of the  $\text{CO}_2$  left in the air after passing over the leaf. This absorbed carbonic acid is determined at the close of the experiment, and we then have all the data for estimating the carbonic acid abstracted from the air by the leaf. The area of the leaf being known, the  $\text{CO}_2$  absorbed can be referred to a unit area of leaf and a unit time.

By the indirect method, which is due to Sachs, the actual increase in dry weight of a given area of an assimilating leaf is determined, and since this increase in weight is due to substances having a definite percentage of carbon, a simple calculation enables us to determine the equivalent amount of carbonic acid abstracted from the air.

By such methods as this it can be shown that an actively assimilating leaf such as that of the *Catalpa* tree, in full daylight, and under favourable conditions of temperature, can take in carbonic acid from the air at the rate of about one-tenth cubic centimetre per hour for each square centimetre of leaf.

Since there are only about three volumes of carbonic acid in 10,000 volumes of ordinary air, this must mean that in a single hour the under surface of the leaf will take in as much carbonic acid as is contained in a column of air about eight feet long, and having the same area of cross section as the leaf.

But this remarkable power of an assimilating leaf will be better appreciated if we compare it with a liquid surface of a strong solution of caustic alkali, which is known to have such a great avidity for carbonic acid.

We can investigate the absorptive power of such solutions for the carbonic acid of the air under fixed and controllable conditions by using a form of apparatus which I have on the table, and which can be examined at the close of the lecture. It is so arranged that an air current of known velocity can be drawn over the surface of the absorbing solution which has a known area.

When a very low velocity of the air current has been reached, the amount of absorption becomes constant at ordinary temperatures at about .17 c.c. of carbonic acid, per square c.m. of surface per hour.

So we see that a leaf, assimilating under natural conditions, is taking in carbonic acid from the air more than half as fast as a surface of the same area would do if it were wetted with a constantly

renewed film of a strong solution of caustic alkali, submitted to a strong current of air.

This is, in itself, a somewhat remarkable conclusion, but what are we to say to a proposition which would limit the absorptive power of the leaf surface to the extremely small apertures of the stomates?

In a leaf such as we have been considering, the aggregate area of the openings of the stomates, when expanded to their widest, amounts to less than *one per cent.* of the total leaf surface, so that if the entry of the  $\text{CO}_2$  takes place exclusively by these openings, we must conclude that it goes in more than fifty times faster than it would do if the mouth of each one of these minute openings were filled with a constantly renewed solution of strong caustic alkali.

Such facts make it difficult unreservedly to accept the view that the gaseous exchanges in leaves are really carried on exclusively by the stomates, which occupy such a small fraction of the leaf surface. On the other hand, the direct experimental evidence in favour of this view is overwhelming, so that we apparently find ourselves on the horns of a dilemma.

There appeared to be only one way out of the difficulty—that was to assume that the leaf knows more about the laws of free diffusion than we do, and has adapted itself to some physical principles which have hitherto escaped notice. This was found to be the case when the structure of the leaf was regarded as a piece of physical apparatus for promoting rapid diffusion.

I do not propose to take you through the various and tedious stages by which the true explanation was reached, but will attempt, as far as possible, to short-circuit the current of the argument.

In the first place, I wish to call your attention to a particular mode of free diffusion which, in gases, has been but little studied, but which has a very direct bearing upon diffusion in the living leaf, where one of the constituents of the diffusing gases, the carbonic acid, is very small in amount compared with the others.

Let us for a moment concentrate our attention on the air which is contained in this open glass cylinder, and endeavour to picture to our minds the jostling crowds of the perfectly elastic molecules of the various gases, flying hither and thither in all imaginable directions, and coming into frequent collision with each other and the sides of the containing vessel.

Now in this jostling throng there is a certain proportion of molecules of *carbonic acid*, which we will imagine for the moment are distinguished from the molecules of the other gases by some difference in colour—let us suppose them to be *green*.

Now, further, consider a plane surface in the contained air of the cylinder; from the dynamical theory of gases it follows that in any given interval of time, temperature and pressure remaining constant, the same average number of the “green” molecules will cross this imaginary plane in opposite directions, and since this will be true

for any plane surface, no matter where we take it within the cylinder, there can be no change in the average distribution of the "green" molecules throughout the cylinder—in other words, no change in any part of the cylinder in the composition of the air as regards its carbonic acid content.

But now let us imagine that the bottom of the cylinder is suddenly made capable of absorbing carbonic acid, say by the introduction, without any disturbance of the air, of a little solution of caustic soda or caustic potash. The "green" molecules which now strike the bottom of the cylinder at all imaginable angles of incidence, will not all rebound, as they originally did, but will be to a large extent trapped in their to-and-fro excursions, so that in the first very brief interval of time a very thin stratum of air, parallel to and immediately above the absorbing surface, will be partially freed from its "green" molecules.

Now consider the kind of exchange of "green" molecules which occurs in the next very brief interval of time between this partially depleted layer at the bottom and the one immediately above it. The rate of exchange across the imaginary plane dividing these two contiguous layers can no longer be equal and opposite, since the number of "green" molecules in the upper stratum is greater than that in the lower. A larger number of the "green" molecules must consequently pass in a given brief interval of time from the higher to the lower stratum than from the lower to the higher; in other words, the *balance of exchange* is in favour of the lower layer. This state of affairs will rapidly propagate itself upwards until the mouth of the cylinder is reached; and provided the air outside the cylinder is kept of the same composition, and the absorptive power of the bottom of the cylinder is also kept constant, the *uncompensated balances of exchange* between the imaginary layers may be regarded as constituting a steady flow or drift of the "green" molecules down the tube towards the absorbent surface.

Although within the column there is this constant flow of carbonic acid molecules in the general direction of the axis of the tube, the system as a whole may now be regarded as static so long as all the conditions remain unchanged. The flow is then strictly analogous to the flow of heat in a bar of metal which is kept with its two ends at a uniform difference of temperature; or to the flow of electricity in a conductor between two regions maintained at a constant difference of potential; and static diffusion admits of precisely the same simple mathematical treatment as these phenomena of conduction of heat and of electricity when we come to its quantitative study.

In such an imaginary experiment as we have been considering, it is clear that the amount of carbonic acid in the air of the cylinder must vary uniformly from a maximum at the top of the cylinder to a vanishing point at the bottom, so that if the  $\text{CO}_2$  really had the green colour, which for purposes of argument we have attributed to it, the

colour of the air column would uniformly diminish from top to bottom.

This can be illustrated by the diffusion of a coloured copper salt down a gelatine column. If this column were cut off just where the colour ceases to be perceptible, and the cut end were immersed in water to carry off the diffusing salt as fast as it came through the column, then if the upper end of the column remained in contact with the coloured copper solution, we should ultimately get a constant steady flow of the salt down the column.

Under these conditions it can be readily shown both experimentally and theoretically, that the actual amount of substance diffusing down the column in a given time will, in the first place, be directly proportional to the difference in the concentration of the diffusing substance at the two ends of the column; it will also be directly proportional to the *area* of cross-section of the column; but inversely proportional to its length.

The fact which for the moment I wish you to bear in mind is that, all other things being the same, the amount of diffusion down a column of this kind *varies directly as the area of the cross-section of the column*.

This is roughly illustrated by these two cylindrical columns of gelatine, of different diameters, down which a coloured solution has been diffusing for equal times.

The salt has penetrated both columns to the same depth, and the gradation of colour is also the same—a proof that the rates of diffusion down the columns must be proportional to their areas of cross-section.

But now let us consider what will happen if, instead of varying the width of the column throughout its entire length, we only partially obstruct the cylinder somewhere in the line of flow, say by means of a thin diaphragm pierced with a single circular hole of less diameter than the bore of the tube.

We must resort to experiment to answer this question.

Suppose we take a series of exactly similar flasks, such as I have here, and produce a steady flow of atmospheric carbonic acid down their necks by partially filling each flask with a solution of caustic soda, the amount of carbonic acid entering the flasks being determined by subsequent titration of the soda solution. We can then study the effect produced by partially obstructing the mouths of the flasks with thin discs of metal or celluloid pierced with a single hole of definite size.

The results of a series of experiments of this kind are given in Table I., and you will see that under these conditions the amounts of carbonic acid diffusing down the cylindrical neck in a given time, are not proportional to the areas of the apertures, as might reasonably have been expected, but are directly proportional to their *diameters*.

TABLE I.—DIFFUSION OF ATMOSPHERIC CO<sub>2</sub> THROUGH SINGLE APERTURES OF VARYING SIZE.

Diam. of Aperture.	CO <sub>2</sub> Diffused Per Hour.	CO <sub>2</sub> Diffused per sq. cm. per Hour.	Ratio of Areas.	Ratio of Diameters.	Ratio of CO <sub>2</sub> Diffused.
mm.	c.c.	c.c.			
22·7	·2380	·0588	1·00	1·00	1·00
6·03	·0625	·2186	·07	·26	·26
3·23	·0398	·4855	·023	·14	·16
2·11	·0260	·8253	·008	·093	·10

This of course implies, that as we make the aperture smaller, the flow through a given unit of its area is proportionally increased—in other words, the acceleration of flow is *inversely proportional to the diameters of the apertures*.

This unexpected fact, which lies at the root of the whole question we are considering to-night, may be experimentally illustrated in a variety of ways.

We may, for instance, cause the aqueous vapour of the air to diffuse into a similar series of flasks, using in this case strong sulphuric acid as the absorbent, and determining the amount of diffusion of the water vapour, by weighing the flasks from time to time. You will see from the results of such an experiment that the diffusion rates again follow pretty closely the ratios of the diameters of the apertures, and are widely divergent from the ratios of areas. (See Table II.)

TABLE II.—DIFFUSION OF AQUEOUS VAPOUR THROUGH APERTURES OF VARYING SIZE.

Diameter of Aperture.	Ratio of Areas.	Ratio of Diameters.	Ratio of Diffusion for Equal Times.
m.m.			
2·117	1·0	1·0	1·0
3·233	2·3	1·52	1·55
5·840	7·6	2·75	2·54

This "diameter law" is also applicable to circular liquid surfaces, the amount of absorption or evaporation from such surfaces varying, under certain conditions, not in accordance with the areas of those surfaces as might have been expected, but with their diameters.

I have here a short burette-like tube with a wide rim of metal round the top. When this tube is completely filled by letting in a solution of caustic soda, we have a circular surface of the solution lying in the same plane as the rim. When this has been exposed to the air for a given time, the carbonic acid absorbed by the disc of liquid can be determined by drawing off and titrating.

If such absorptive discs of different dimensions are exposed to air which is in *slight movement*, we shall find that the carbonic acid absorbed is proportional to the *area* of the surface. The smaller, however, we make the discs, and the greater precautions we take to keep the air over them perfectly still, the nearer do the absorptions become proportional to the diameters. (See Table III.)

TABLE III.—ABSORPTION OF ATMOSPHERIC CO<sub>2</sub> BY CIRCULAR SURFACES OF SOLUTIONS OF CAUSTIC ALKALI.

Diameter of Surface.	Ratio of Areas.	Ratio of Diameters.	Mean Ratio of Areas and Diameters.	Ratio of CO <sub>2</sub> Absorbed.
mm.				
10·25	1·0	1·0	1·0	1·0
20·25	3·9	1·9	2·9	3·0
29·25	8·1	2·8	5·4	5·3
40·00	15·2	3·9	9·5	9·2
5·00	1·0	1·0	..	1·0
10·25	4·2	2·05	..	2·47

There is always, however, more difficulty in obtaining these results with plane absorbing surfaces, than by diffusion through a perforated diaphragm. The reason for this will be apparent later.

Before entering on an explanation of these facts, I wish you to note a very important conclusion to be drawn from them, and one which readily admits of experimental verification.

We have seen that when we partially obstruct the diffusive flow of a gas or liquid by a thin septum with a single circular perforation, the velocity of the flow through each unit area of aperture increases as the diameter of the aperture decreases. One might therefore expect that if a number of fine holes were suitably arranged in such a septum, the acceleration of flow through the individual holes might assume such proportions that a perforated septum of this kind would exercise little or no obstruction on the diffusive flow, although in such a case the aggregate area of the holes might only represent a small fraction of the total area of the obstructing septum.

Strange and paradoxical as such a conclusion may at first sight appear, it will bear the test of experiment.

I have here a thin film of celluloid—in fact, a piece of the ordinary Kodak roller-film. This has been perforated with holes about  $\cdot 4$  millimetre in diameter, arranged at a little more than  $2\cdot 5$  diameters apart, so that there are just 100 of such perforations on a square centimetre of area. The clear holes represent about one-tenth of the area of the film, nine-tenths of the sieve being blocked up with impervious celluloid.

Here are two columns of gelatine, down which a blue solution of copper-ammonium sulphate have been diffusing for equal times. One of these columns is unobstructed in any way, being in direct contact with the coloured liquid. In the other case a finely perforated celluloid film has been interposed, which has the effect of blocking out nine-tenths of the cross-section of the column. You see that, notwithstanding this, there is no appreciable difference in the amounts of coloured salt which have diffused in the two cases; the salt has, in fact, gone through the finely pierced septum as readily as if no obstruction were present.

(N.B.—The celluloid film is itself not permeable.)

We find that exactly the same holds good with gaseous diffusion.

If finely perforated septa of this kind are luted on to short tubes containing caustic soda and are exposed to still air, the amount of carbonic acid diffusing through the holes in the diaphragm can be compared with the amount which we know would diffuse down the open tube under like conditions.

Some results of this kind are given in Table IV.

TABLE IV.—DIFFUSION OF ATMOSPHERIC  $\text{CO}_2$  THROUGH MULTIPERFORATE SEPTA INTO TUBE 4 CM. LONG. DIAM. OF HOLES  $\cdot 380$  MM.

No. of Holes per Square cm.	Diameters Apart.	$\text{CO}_2$ Diffusing through Septum per Hour.	Open Tube, Diffusion per Hour.	Percentage of Septum Diffusion on Open Tube Diffusion.	Percentage, Area of Cross-section occupied by Holes.
100·00	2·63	c.c. ·361	c.c. ·346	104·3	11·34
25·00	5·26	·148	·342	43·2	2·82
11·11	7·8	·131	·352	37·2	1·25
6·25	10·52	·110	·353	31·1	·70
15·7	15·7	·068	·334	20·4	·31

I must now ask you to follow me in a somewhat theoretical excursion in quest of an explanation of these curious facts.

We have seen that when steady diffusion is going on down a cylindrical column which is absorbent at the bottom, there is a

uniform diminution in the density of the diffusing substance from one end of the column to the other, evidenced in the case of a coloured substance by a gradual and uniform thinning out of the colour in the direction of the axis of the column. But in any horizontal cross-section of the column, the colour is of the same intensity in all parts of the section, which means of course that the diffusing substance is of equal density along these planes.

In a diagrammatic section of such a column we should therefore represent the surfaces of equal density by straight lines drawn at right angles to the axis of the cylinder, and the stream lines of the diffusing substance by straight lines drawn parallel to the axis.

I am able to show you the horizontal lines of equal density in a cylinder, produced by a process of intermittent diffusion presently to be described.

When diffusion goes on into a flat absorbent disc, or aperture, instead of into a cylinder, it is clear that the stream lines of the diffusing substance must strongly converge towards the disc, instead of moving vertically downwards as they do in the cylinder, and it is also clear that the lines or surfaces of equal density in the diffusing substance, must form curved surfaces of some kind over the disc. We must now consider the exact form which those lines and surfaces will take.

It so happens that there is a problem in electrostatics which is analogous to the one before us, and it is one which has been fully worked out by mathematical physicists.

When an insulated conductor receives an electric charge, the form taken by the surfaces of equi-potential around the conductor depends on its shape, and on the nature and distribution of other charges in its neighbourhood.

If we suppose the absorbing disc or perforation used in our diffusion experiments to be replaced by an electrified disc of similar dimensions, embedded flush in a wide non-conducting rim, then the surfaces of equal electric potential in the air above the disc will take the form represented in Fig. 1. The surfaces will form a series of *hemi-spheroids* which in any vertical section passing through the centre of the disc will give a series of ellipses, having their common foci in the edges of the disc. Faraday's lines or tubes of force on the other hand will, in this case, be represented by a series of hyperbolas, also having their foci in the edges of the disc.

Now we have every reason to believe that in a diffusion experiment with an absorbent disc the surfaces of equal density of the diffusing substance over the disc are the exact analogues of the surfaces of equal potential over the similar electrified disc, and that the stream lines of the diffusing substance are the analogues of the lines or tubes of force. If this be so, the diagram will equally well represent an experiment in which, for instance, the carbonic acid of perfectly still air is being absorbed by a disc of soda solution, surrounded by a wide rim.



Fig. 2 represents what we might expect to be the state of things when diffusion takes place through a circular aperture in a diaphragm. Here the stream lines of the substance, which are convergent as they approach the aperture, diverge again when the opening is past, and we should expect to get a double system of the ellipsoidal zones of equal density on either side of the aperture.

Did time admit I could show you that this hypothesis is not only capable of giving reasonable and consistent explanations of all the phenomena of diffusion into and through apertures, but completely explains the "diameter law" and also enables us to predict the amount of gas, vapour, or solute which will pass under given conditions, and the results can be verified by experiment.

I have only time to glance at one or two readily verifiable deductions from this hypothesis. In the first place it fully accounts for what I have called the "diameter law," that is to say that diffusion through circular apertures in a diaphragm is proportional to their diameters, not to their areas.

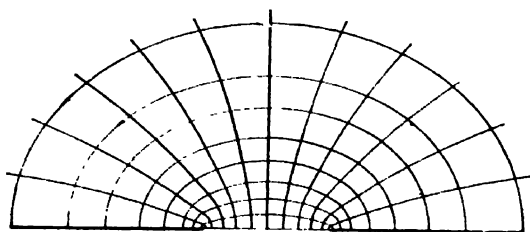
In two diagrams on the wall we have represented the arrangement of the equi-density curves and stream lines over two absorbent discs, one double the diameter of the other. We may take these discs to represent an alkaline solution absorbing carbonic acid from the air.

The two systems are on the same relative scale, one in fact being the image of the other magnified by two diameters.

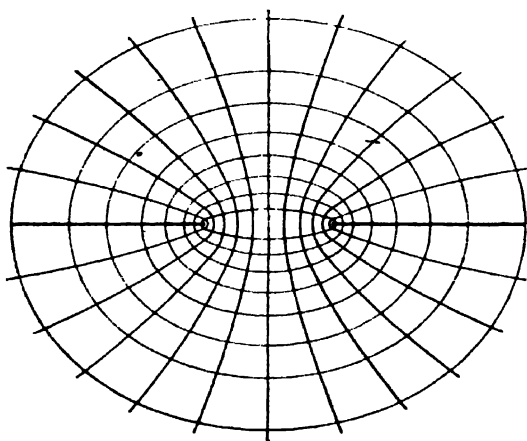
It will be seen that a curved line corresponding to any given actual density of the diffusing substance must be twice as far from the surface of the larger disc as it is from the surface of the smaller; that is to say, the *gradient of density* on which the flow depends, is twice as steep over the small disc as it is over the large one. From this it follows that for equal areas the flow into the smaller disc is twice that into the larger, and that the *total* flow must be proportional to the diameters, which is just what is found to be the case.

Wherever we get conditions favourable for the formation of a system of equi-density zones on one or both sides of a perforated diaphragm, diffusion will go on in accordance with this "diameter law." But one system of zones is quite sufficient for the purpose, so that in a case like that of Fig. 2, which represents the course of diffusion of atmospheric  $\text{CO}_2$  in perfectly still air into an absorbent chamber, we might allow the outer system of equi-density shells over the aperture to be completely swept away by air currents and still the "diameter law" would hold good on account of the inner series of zones, which, from their position, are protected from the air currents. This explains in a very satisfactory manner why it is much more easy to demonstrate the diameter law with apertures in a diaphragm, than simply with absorbing discs, where only one external system of equi-density shells can exist, which is of course extremely liable to be influenced by disturbing currents.

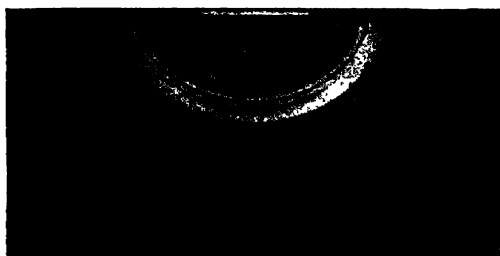
Satisfactory, however, as this hypothesis is in explaining every-



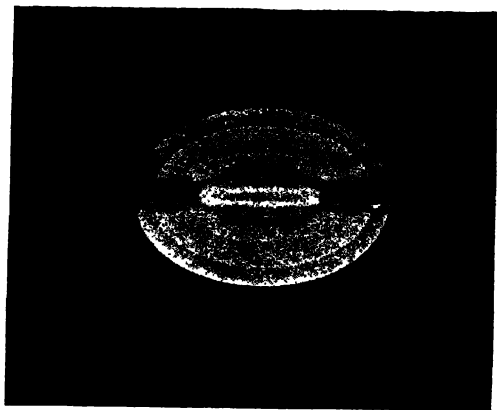
**FIG. 1.**



**FIG. 2.**



**FIG. 3.**



**FIG. 4.**

thing connected with these curious facts of diffusion, it must be borne in mind that the reasoning on which it is based is in part deductive and in part dependent on an analogy.

Nearly 300 years ago it was said by Sir Thomas Roe that "many things hold well in discourse, and in the theorique, satisfie curious imaginations, but in practice and execution are found difficult and ayrie."

Fortunately this does not apply to the present case, and I am able to bring before you this evening for the first time an experimental demonstration of the existence of zones of equal density in the neighbourhood of an aperture through which diffusion is going on, and to show you that they have the exact shape which the theory requires.

I have here a rectangular glass cell divided horizontally by a thin plate of celluloid having a circular hole punched through it. The lower half of the cell is filled with a solution of gelatine containing a little barium chloride, and the upper half with a solution of sodium sulphate.

The relative strengths of the solutions are so adjusted that the two salts, diffusing in opposite directions through the aperture, shall meet somewhere in the gelatine where a precipitate of barium sulphate is thrown down at the surfaces of contact of the two opposing streams of diffusion. The result is that we get a slowly growing spheroidal mass of precipitate, starting from the aperture, and resembling in shape the head of an inverted mushroom.

If we arrange for the diffusion of the sodium sulphate to be intermittent, or better still if we alternate the diffusion of a sulphate with that of a chromate, we get well marked *zonings* in the precipitate forming the spheroid, *zonings* which correspond to the successive forms which the spheroid has assumed during growth, and which therefore must have been zones of equal density of the diffusing substances. We can study the forms which these assume in relation to the aperture by subsequently cutting sections through the gelatine, but by a little arrangement we can make the apparatus cut its own sections as the diffusion goes on.

This is done by making the aperture in the diaphragm *semi-circular* instead of circular, and bringing its straight edge close up to the side of the glass vessel.

I will now throw on the screen some photographs of vertical sections of spheroids of diffusion of this kind. (See Figs. 3 and 4.)

On comparing the lines of equal density around the aperture with the diagrams on the wall, you will at once see that their shape is exactly that required by theory—they describe a series of ellipses having their common foci in the edges of the aperture through which the diffusion is taking place.

The actual stream lines of the diffusing substance are not visible, but as these must necessarily be normal to the curves of equal density, they can only be represented by a series of hyperbolas, also having their foci in the edges of the aperture.

The electrostatic analogy which has served so well in determining the form of the zones of equal density around single apertures may also be used for predicting their distribution around a series of apertures in a diaphragm.

If we regard the individual holes in a multiperforate diaphragm as so many minute discs, all electrified to a common potential, the lines of equi-potential and the lines of force should take a form something like that represented in the diagram (see Fig. 5), the lines of equi-potential forming complete ellipses in the immediate neighbourhood of the electrified discs, but gradually intersecting and forming a series of wavy lines which become more and more horizontal as the distance gets more remote.

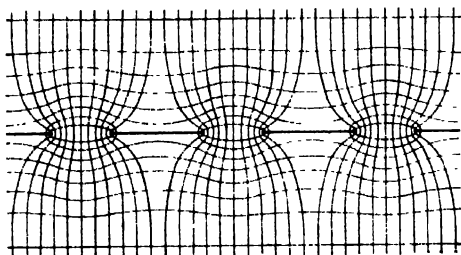
Could they be rendered visible, these are also the forms which we should expect the lines of equal density of a substance to take when it is diffusing through a series of small apertures. I am able to give you a verification of this, by throwing on the screen a photograph showing the result of intermittent diffusion through a series of such apertures. (See Figs. 6 and 7.) The lines of equal density are marked out by the alternate bands of sulphate and chromate of barium, as they were in the last experiment.

From the shape of these lines of equal density it is possible to determine the form of the stream lines of the diffusing substance, and to show that the tendency of a multiperforate septum of this kind, is to locally increase the gradient of density in its neighbourhood and so to accelerate the flow through the small apertures. We get, in fact, a complete and satisfactory explanation of the small amount of obstruction which such a diaphragm produces, when put in the way of a diffusive flow of gas or liquid.

Intermittent diffusion, such as I have described, may be used to illustrate in a variety of ways the distribution of electrical potential around electrified bodies which are within the sphere of each other's action.

It is generally a difficult and laborious task to work out the distribution of the surfaces of equi-potential around electrified bodies which are near enough to influence each other. By this system of intermittent diffusion we may sometimes make nature work out the problem for us. Here, for instance (see Fig. 8), is a figure copied from Clerk Maxwell's 'Electricity and Magnetism,' representing the form which is assumed by equi-potential surfaces around two points, charged with quantities of electricity of the same kind in the ratio of four to one. If the analogy is correct, diffusion through apertures having their diameters in the ratio of two to one, ought to give the same series of figures. You see from the photograph of an actual experiment given in Fig. 9 that this supposition is correct.

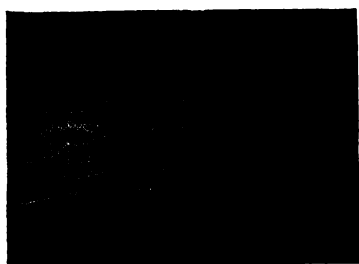
In Fig. 10 are given the calculated lines of force at the edges of two parallel plates, one of which is insulated and electrified, the other connected with the earth. These ought to correspond in shape to the equi-density lines of a substance undergoing steady diffusion



**FIG. 5.**



**FIG. 6.**



**FIG. 7.**

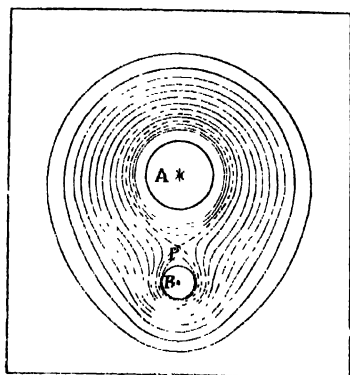


FIG. 8.

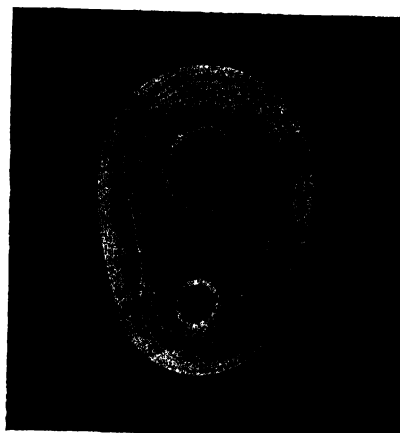


FIG. 9.

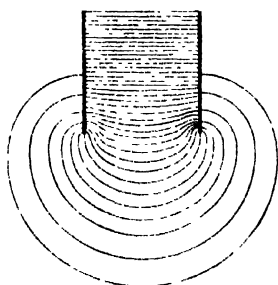


FIG. 10.

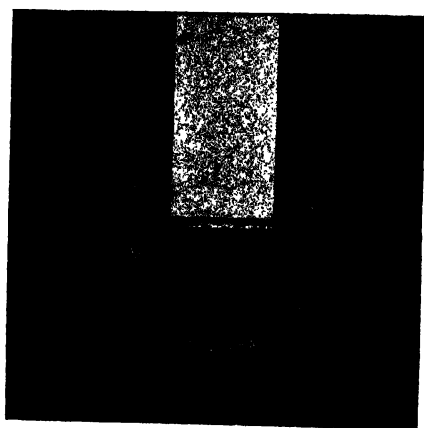


FIG. 11.

from between two parallel plates, as in fact you see they do. (See Fig. 11.)

But considerations of this kind, although of interest in showing the striking analogies between certain phenomena of electrostatics and static diffusion, would carry me too far from my main object, and I must again bring you back to the green leaf, which was the starting-point of my lecture.

If we regard the structure of the leaf from the new point of view which now suggests itself, we can readily understand how it is that the stomates, notwithstanding the relatively small area of the leaf surface which they occupy, can drink in the atmospheric carbonic acid with such rapidity.

The finely perforated epidermis of the leaf, tightly stretched over the interior air-spaces whose walls can absorb carbonic acid, constitutes a multiperforate septum which is under the most favourable conditions to produce an acceleration of the diffusive flow of the gas into the leaf.

The laws of gaseous diffusion through small apertures are now so well understood that we can predict with certainty the particular quantitative effect produced on a given diffusive flow by any screen with perforations of known size and distribution providing they are not within a certain number of diameters distant from each other. These deductions can be verified by experimenting with small shallow glass cylinders, made absorbent inside, and closed at the top with very thin discs of celluloid perforated in a known manner. Such a piece of apparatus may be regarded as an artificial leaf, the perforated celluloid representing the epidermis with its stomates, whilst the absorbing solution of caustic soda acts the part of the assimilating centres.

Having obtained confidence in the accuracy of the method of calculation, we can then apply the same principles to determining the efficiency of the leaf stomates, when the whole system is regarded as a piece of mechanism for promoting diffusion.

In the first place, it is found experimentally that the most economical arrangement of very small apertures is to have them set about 8 or 10 diameters apart, for at that distance the interference with each other practically ceases. *This is about the distance at which we generally find the stomates arranged on the underside of most leaves.*

You will remember that the amount of atmospheric carbonic acid which enters an assimilating leaf in an hour, is about  $\cdot 1$  c.c. for every square centimetre of leaf. Now it can be shown that for this amount of gas to enter through the stomates it is only necessary for the  $\text{CO}_2$  content of the air just within the leaf to be kept down to  $2\cdot 8$  parts per 10,000, when that of the outer air is three parts per 10,000. This very slight difference in the partial pressure within and without is quite sufficient to account for all the entering  $\text{CO}_2$ , thanks to the special structure of the leaf.

Thus all the apparent difficulties in the way of accepting the



minute stomates as the sole pathways of gaseous exchange in the leaf entirely disappear when the leaf is studied in this new light, and it becomes evident that the adjustment of the mechanism of the leaf to the physical properties of its surrounding medium is far more perfect than has been hitherto suspected. The leaves of plants have in fact proved themselves better physicists than ourselves, since their structure bears the impress of response to certain properties of gases of which we have hitherto been ignorant.

This is by no means the first occasion on which the plant has given us a lead in physics. The theory of dilute solutions, formulated by Van't Hoff, and indicating that the laws of Boyle and of Avogadro are as applicable to dilute solutions as they are to gases, had its origin in the observations of De Vries and of Pfeffer on the plasmolysis of living cells and the properties of natural semi-permeable membranes.

Nor can we doubt that there are many more such instances which only await detection, and we may reasonably hope that the boundaries of physics and of chemistry will be materially enlarged in unexpected directions if we pay due regard to the whispered hints and slender clues which are on all sides given by the living world of Nature.

[H. T. B.]

Friday, March 29, 1901.

The RIGHT HON. SIR JAMES STIRLING, M.A. LL.D.,  
Vice-President, in the Chair.

The RIGHT HON. LORD RAYLEIGH, M.A. D.C.L. LL.D. F.R.S. M.R.I.  
PROFESSOR OF NATURAL PHILOSOPHY R.I.

*Polish.*

THE lecture commenced with a description of a home-made spectro-scope of considerable power. The lens, a plano-convex of 6 inches aperture and 22 feet focus, received the rays from the slit, and finally returned them to a pure spectrum formed in the neighbourhood. The body of the prism was of lead; the faces, inclined at  $70^\circ$ , were of thick plate-glass cemented with glue and treacle. It was charged with bisulphide of carbon, of which the free surface (of small area) was raised above the operative part of the fluid. The prism was traversed twice, and the effective thickness was  $5\frac{1}{2}$  inches, so that the resolving power corresponded to 11 inches, or 28 cm., of  $\text{CS}_2$ . The liquid was stirred by a perforated triangular plate, nearly fitting the prism, which could be actuated by means of a thread within reach of the observer. The reflector was a *flat*, chemically silvered in front.

So far as eye observations were concerned, the performance was satisfactory, falling but little short of theoretical perfection. The stirrer needed to be in almost constant operation, the definition usually beginning to fail within about 20 seconds after stopping the stirrer. But although the stirrer was quite successful in maintaining uniformity of temperature as regards *space*, i.e. throughout the dispersing fluid, the temperature was usually somewhat rapidly variable with *time*, so that photographs, requiring more than a few seconds of exposure, showed inferiority. In this respect a grating is more manageable.

The lens and the faces of the prism were ground and polished (in 1893) upon a machine kindly presented by Dr. Common. The flat surfaces were tested with a spherometer, in which a movement of the central screw through  $\frac{1}{100000}$  inch could usually be detected by the touch. The external surfaces of the prism faces were the only ones requiring accurate flatness. In polishing, the operation was not carried as far as would be expected of a professional optician. A

few residual pittings, although they spoil the appearance of a surface, do not interfere with its performance, at least for many purposes.

In the process of grinding together two glass surfaces, the particles of emery, even the finest, appear to act by *pitting* the glasses, i.e. by breaking out small fragments. In order to save time and loss of accuracy in the polishing, it is desirable to carry the grinding process as far as possible, using towards the close only the finest emery. The limit in this direction appears to depend upon the tendency of the glasses (6 inches diameter) to *seize*, when they approach too closely, but with a little care it is easy to attain such a fineness that a candle is seen reflected at an angle of incidence not exceeding  $60^\circ$ , measured as usual from the perpendicular.

The fineness necessary, in order that a surface may reflect and refract regularly without diffusion, viz. in order that it may appear *polished*, depends upon the wave-length of the light and upon the angle of incidence. At a grazing incidence all surfaces behave as if polished, and a surface which reflects red light pretty well may fail signally when tested with blue light at the same angle. If we consider incidences not too far removed from the perpendicular, the theory of gratings teaches that a regularly corrugated surface behaves as if absolutely plane, provided that the *wave-length* of the corrugations is less than the wave-length of the light, and this without regard to the *depth* of the corrugations. Experimental illustrations, drawn from the sister science of Acoustics, were given. The source was a bird-call from which issued vibrations having a wave-length of about 1.5 cm., and the percipient was a high-pressure sensitive flame. When the bird-call was turned away, the flame was silent, but it roared vigorously when the vibrations were reflected back upon it from a plate of glass. A second plate, upon which small pebbles had been glued so as to constitute an ideally rough surface, acted nearly as well, and so did a piece of tin plate suitably corrugated. In all these cases the reflection was *regular*, the flame becoming quiet when the plates were turned out of adjustment through a very small angle. In another method of experimenting the incidence was absolutely perpendicular, the flame being exposed to both the incident and the reflected waves. It is known that under these circumstances the flame remains quiescent at the *nodes* and flares most vigorously at the *loops*. As the reflector is drawn slowly back, the flame passes alternately through the nodes and loops, thus executing a cycle of changes as the reflector moves through *half* a wave-length. The effects observed were just the same whether the reflector were smooth or covered with pebbles, or whether the corrugated tin plate were substituted. All surfaces were smooth *enough* in relation to the wave-length of the vibration to give substantially a specular reflexion.

Finely-ground surfaces are still too coarse for perpendicular specular reflexion of the longest visible waves of light. Here the material may be metal, or glass silvered chemically on the face subsequently to the grinding. But experiment is not limited by the

capabilities of the eye; and it seems certain that a finely ground surface would be smooth enough to reflect without sensible diffusion the longest waves, such as those found by Rubens to be nearly 100 longer than the waves of red light. An experiment may be tried with radiation from a Leslie cube containing hot water, or from a Welsbach mantle (without a chimney). In the lecture the latter was employed, and it fell first at an angle of about  $45^\circ$  upon a finely ground flat glass silvered in front. By this preliminary reflection, the radiation was purified from waves other than those of considerable wave-length. The second reflection (also at  $45^\circ$ ) was alternately from polished and finely ground silvered surfaces of the same size, so mounted as to permit the accurate substitution of the one for the other. The heating-power of the radiation thus twice reflected was tested with a thermopile in the usual manner. Repeated comparisons proved that the reflection from the ground surface was about .76 of that from the polished surface, showing that the ground surface reflected the waves falling upon it with comparatively little diffusion. A slight rotation of any of the surfaces from their proper positions at once cut off the effect. It is probable that the device of submitting radiation to preliminary reflections from one or more merely ground surfaces might be found useful in experiments upon the longest waves.

In view of these phenomena we recognise that it is something of an accident that polishing processes, as distinct from grinding, are needed at all; and we may be tempted to infer that there is no essential difference between the operations. This appears to have been the opinion of Herschel,\* whom we may regard as one of the first authorities on such a subject. But, although, perhaps, no sure conclusion can be demonstrated, the balance of evidence appears to point in the opposite direction. It is true that the same powders may be employed in both cases. In one experiment a glass surface was polished with the same emery as had been used effectively a little earlier in the grinding. The difference is in the character of the backing. In grinding, the emery is backed by a hard surface, e.g. of glass, while during the polishing the powder (mostly rouge in these experiments) is imbedded in a comparatively yielding sub-

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\* Enc. Met., Art. Light, p. 447, 1830: "The intensity and regularity of reflection at the external surface of a medium is found to depend not merely on the nature of the medium, but very essentially on the degree of smoothness and polish of its surface. But it may reasonably be asked, how any regular reflection can take place on a surface polished by art, when we recollect that the process of polishing is, in fact, nothing more than grinding down large asperities into smaller ones by the use of hard gritty powders, which, whatever degree of mechanical comminution we may give them, are yet vast masses, in comparison with the ultimate molecules of matter, and their action can only be considered as an irregular tearing up by the roots of every projection that may occur in the surface. So that, in fact, a surface artificially polished must bear somewhat of the same kind of relation to the surface of a liquid, or a crystal, that a ploughed field does to the most delicately polished mirror, the work of human hands."

stance, such as pitch. Under these conditions, which preclude more than a moderate pressure, it seems probable that no pits are formed by the breaking out of fragments, but that the material is worn away (at first, of course, on the eminences) almost molecularly.

The progress of the operation is easily watched with a microscope, provided, say, with a  $\frac{1}{4}$ -inch object-glass. The first few minutes suffice to effect a very visible change. Under the microscope it is seen that little facets, parallel to the general plane of the surface, have been formed on all the more prominent eminences.\* The facets, although at this stage but a very small fraction of the whole area, are adequate to give a sensible specular reflection, even at perpendicular incidence. On one occasion five minutes' polishing of a rather finely ground glass surface was enough to qualify it for the formation of interference bands, when brought into juxtaposition with another polished surface, the light being either white or from a soda flame; so that in this way an optical test can be applied almost before the polishing has begun.†

As the polishing proceeds, the facets are seen under the microscope to increase both in number and in size, until they occupy much the larger part of the area. Somewhat later the parts as yet untouched by the polisher appear as pits, or spots, upon a surface otherwise invisible. Fig. 1 represents a photograph of a surface at this stage taken with the microscope. The completion of the process consists in rubbing away the whole surface down to the level of the deepest pits. The last part of the operation, while it occupies a great deal of time, and entails further risk of losing the "truth" of the surface, adds very little to the effective area, or to the intensity of the light regularly reflected or refracted.

Perhaps the most important fact taught by the microscope is that the polish of individual parts of the surface does not improve during the process. As soon as they can be observed at all, the facets appear absolutely structureless. In its subsequent action the polishing tool, bearing only upon the parts already polished, extends the boundary of these parts, but does not enhance their quality. Of course, the mere fact that no structure can be perceived does not of itself prove that pittings may not be taking place of a character too fine to be shown by a particular microscope or by any possible microscope. But so much discontinuity, as compared with the grinding action, has to be admitted in any case, that one is inevitably led to the conclusion that in all probability the operation is a molecular one, and that no coherent fragments containing a large number of molecules are broken out. If this be so, there would be much less difference

\* The interpretation is facilitated by a thin coating of aniline dye which attaches itself mainly to the hollows.

† With oblique incidence, as in Talbot's experiments (see *Phil. Mag.*, xxviii. p. 191, 1889), achromatic bands may be observed from a surface absolutely unpolished, but this disposition would not be favourable for testing purposes.

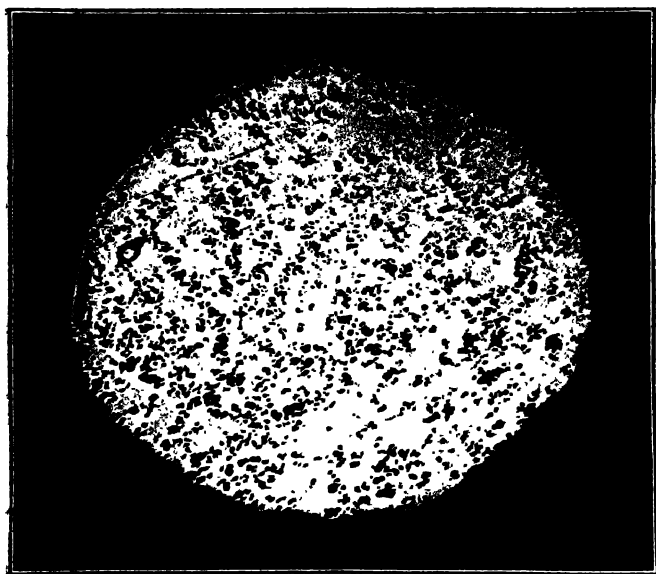


FIG. 1.

than Herschel thought between the surfaces of a polished solid and of a liquid.

Several trials have been made to determine how much material is actually removed during the polishing of glass. In one experiment a piece 6 inches in diameter, very finely ground, was carefully weighed at intervals during the process. Losses of .070, .032, .045, .026, .032 gms. were successively registered, amounting in all to .205 gms. Taking the specific gravity of the glass as 3, this corresponds to a thickness of  $3.6 \times 10^{-4}$  cm., or to about 6 wave-lengths of mean light, and it expresses the distance between the original *mean* surface and the final plane. But the polish of this glass, though sufficient for most practical purposes, was by no means perfect. Probably the 6 wave-lengths would have needed to be raised to 10 in order to satisfy a critical eye. It may be interesting to note for comparison that, in the grinding, one charge of emery, such as had remained suspended in water for seven or eight minutes, removed a thickness of glass corresponding to 2 wave-lengths.

In other experiments the thickness removed in polishing was determined optically. A very finely ground disc was mounted in the lathe and polished locally in rings. Much care was needed to obtain the desired effect of a ring showing a continuously increasing polish from the edges inwards. To this end it was necessary to keep the polisher (a piece of wood covered with resin and rouge) in constant motion, otherwise a number of narrow grooves developed themselves.

The best ring was about half an inch wide. When brought into contact with a polished flat and examined at perpendicular incidence with light from a soda flame, the depression at its deepest part gave a displacement of three bands, corresponding to a depth of  $1\frac{1}{2}\lambda$ . On a casual inspection this central part appeared well polished, but examination under the microscope revealed a fair number of small pits. Further working increased the maximum depth to  $2\frac{1}{2}\lambda$ , when but very few pits remained. In this case, then, polish was effected during a lowering of the mean surface through 2 or 3 wave-lengths, but the grinding had been exceptionally fine.

It may be well to emphasise that the observations here recorded relate to a *hard* substance. In the polishing of a soft substance, such as copper, it is possible that material may be loosened from its original position without becoming detached. In such a case pits may be actually filled in, by which the operation would be much quickened. Nothing suggestive of this effect has been observed in experiments upon glass.

Another method of operating upon glass is by means of hydrofluoric acid. Contrary to what is generally supposed, this action is extremely regular, if proper precautions are taken. The acid should be weak, say one part of commercial acid to two hundred of water, and it should be kept in constant motion by a suitable rocking arrangement. The parts of the glass not intended to be eaten into are, as usual, protected with wax. The effect upon a polished flat

surface is observed by the formation of Newton's rings with soda light. After perhaps three-quarters of an hour, the depression corresponds to half a band, i.e. amounts to  $\frac{1}{2}\lambda$ , and it appears to be uniform over the whole surface exposed. Two pieces of plate glass, 3 inches square, and flat enough to come into fair contact all over, were painted with wax in parallel stripes, and submitted to the acid for such a time, previously ascertained, as would ensure an action upon the exposed parts of  $\frac{1}{2}\lambda$ . After removal of the wax, the two plates, crossed and pressed into contact so as to develop the colours, say of the second order, exhibited a chess-board pattern. Where two uncorroded, or where two corroded parts, are in contact, the colours are nearly the same, but where a corroded and an uncorroded surface overlap, a strongly contrasted colour is developed. The combination lends itself to lantern projection, and the pattern upon the screen [shown] is very beautiful, if proper precautions are taken to eliminate the white light reflected from the first and fourth surfaces of the plates.

In illustration of the action of hydrofluoric acid, photographs\* were shown of interference bands as formed by soda-light between glass surfaces, one optically flat and the other ordinary plate, upon which a drop of dilute acid had been allowed to stand (Fig. 2). Truly plane surfaces would give bands straight, parallel, and equidistant.

Hydrofluoric acid has been employed with some success to correct ascertained errors in optical surfaces. But while improvements in actual optical performance have been effected, the general appearance of a surface so treated is unprepossessing. The development of latent scratches has been described on a former occasion.†

A second obvious application of hydrofluoric acid has hitherto been less successful. If a suitable stopping could be found by which the deeper pits could be protected from the action, corrosion by acid could be used in substitution for a large part of the usual process of polishing.

In connection with experiments of this sort, trial was made of the action of the acid upon finely ground glass, such for example as is used as a backing for stereoscopic transparencies, and very curious results were observed. For this purpose the acid may conveniently be used much stronger, say one part of commercial acid to 10 parts of water, and the action may be prolonged for hours or days. The general appearance of the glass after treatment is smoother and more translucent, but it is only under the microscope that the remarkable changes which the surface has undergone become intelligible. Fig. 3 is from a photograph taken in the microscope, the focus being upon the originally ground surface itself. The whole area is seen to be divided into cells. These cells increase as the action progresses, the

\* The plates were sensitised in the laboratory with cyanine.

† Proc. Roy. Inst., March 1893.



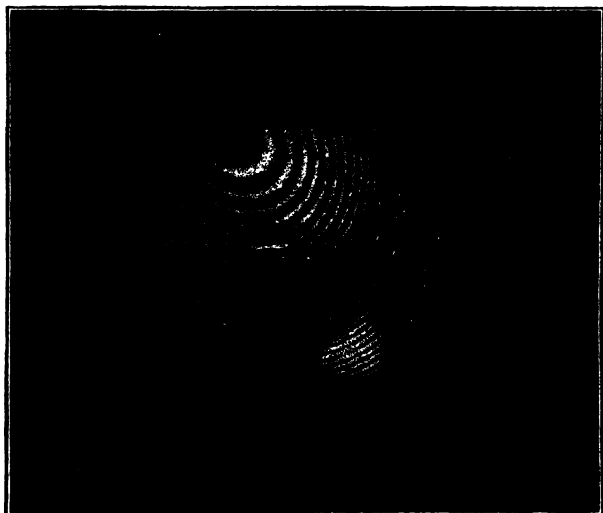


FIG. 2.

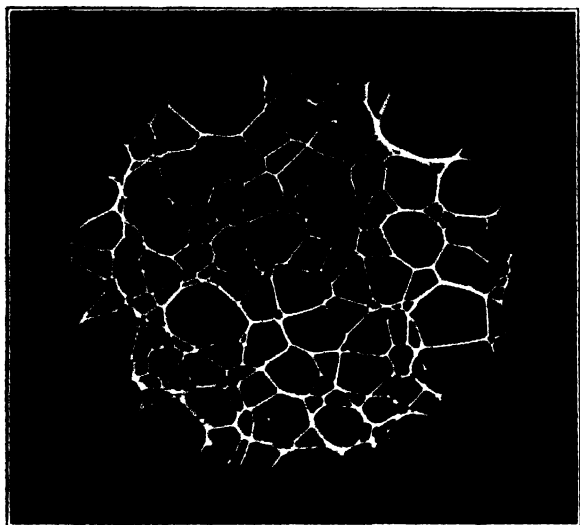


FIG. 3.

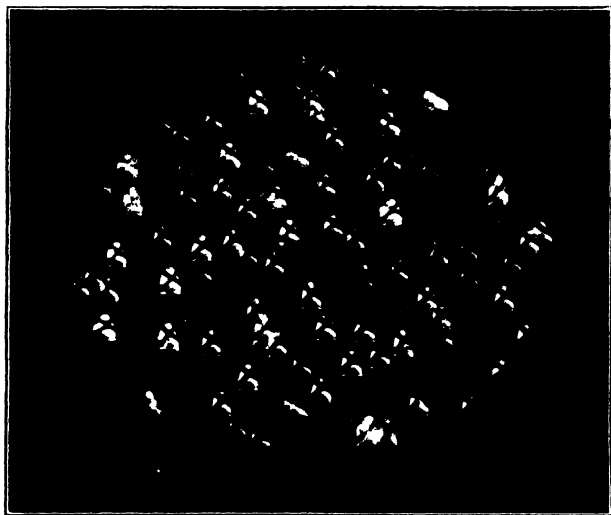


FIG. 4.

smaller ones being, as it were, eaten up by the bigger. The division lines between the cells are *ridges*, raised above the general level, and when seen in good focus appear absolutely sharp. The general surface within the cells shows no structure, being as invisible as if highly polished.

That each cell is in fact a concave lens, forming a separate image of the source of light, is shown by slightly screwing out the object-glass. Fig. 4 was taken in this way from the same surface, the source of light being the flame of a paraffin lamp, in front of which was placed a cross cut from sheet-metal.

The movement required to pass from the ridge to the image of the source, equal to the focal length ( $f$ ) of the lens, may be utilised to determine the depth ( $t$ ) of a cell. In one experiment the necessary

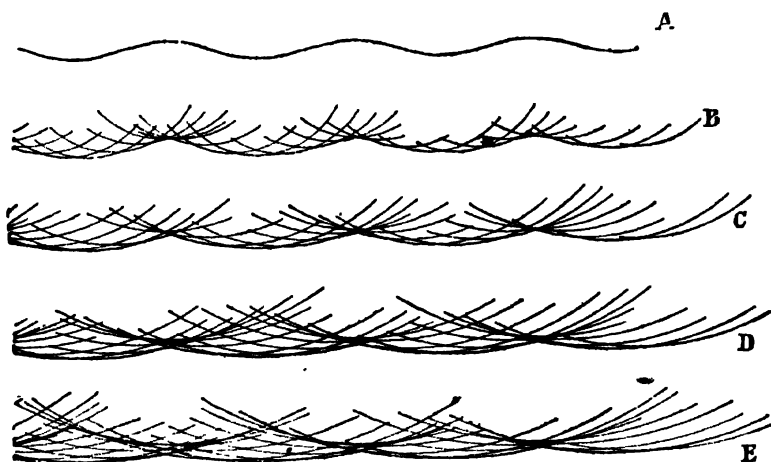


FIG. 5.

movement was  $\cdot 005$  inch. The semi-aperture ( $y$ ) of the "lens" was  $\cdot 0015$  inch, whence by the formula  $y^2 = ft$ , we find  $t = \cdot 00045$  inch. This represents the depth of the cell, and it amounts to about 8 wave-lengths of yellow light.

The action of the acid seems to be readily explained if we make the very natural supposition that it eats in everywhere, at a fixed rate, normally to the actual surface. If the amount of the normal corrosion after a proposed time be known, the new surface can be constructed as the "envelope" of spheres having the radius in question and centres distributed over the old surface. Ultimately, the new surface becomes identified with a series of spherical segments having their centres at the deeper pits of the original surface. The construction is easily illustrated in the case of two dimensions. In the figure

A is supposed to be the original surface ; B, C, D, E surfaces formed by corrosion, being constructed by circles having their centres on A. In B the ridges are still somewhat rounded, but they become sharp in D and E. The general tendency is to sharpen elevations and to smooth off depressions.

Friday, April 19, 1901.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

PROFESSOR J. J. THOMSON, M.A. Sc.D. F.R.S.

*The Existence of Bodies Smaller than Atoms.*

THE masses of the atoms of the various gases were first investigated about thirty years ago by methods due to Loschmidt, Johnstone Stoney and Lord Kelvin. These physicists, using the principles of the kinetic theory of gases, and making certain assumptions (which it must be admitted are not entirely satisfactory) as to the shape of the atom, determined the mass of an atom of a gas; and when once the mass of an atom of one substance is known the masses of the atoms of all other substances are easily deduced by well-known chemical considerations. The results of these investigations might be thought to leave not much room for the existence of anything smaller than ordinary atoms, for they showed that in a cubic centimetre of gas at atmospheric pressure and at 0° C. there are about 20 million, million, million ( $2 \times 10^{21}$ ) molecules of the gas.

Though some of the arguments used to get this result are open to question, the result itself has been confirmed by considerations of quite a different kind. Thus, Lord Rayleigh has shown that this number of molecules per cubic centimetre gives about the right value for the optical opacity of the air; while a method which I will now describe, by which we can directly measure the number of molecules in a gas, leads to a result almost identical with that of Loschmidt. This method is founded on Faraday's laws of electrolysis; we deduce from these laws that the current through an electrolyte is carried by the atoms of the electrolyte, and that all these atoms carry the same charge, so that the weight of the atoms required to carry a given quantity of electricity is proportional to the quantity carried. We know too, by the results of experiments on electrolysis, that to carry the unit charge of electricity requires a collection of atoms of hydrogen which together weigh about one-tenth of a milligram; hence, if we can measure the charge of electricity on an atom of hydrogen, we see that one-tenth of this charge will be the weight in milligrams of the atom of hydrogen. This result is for the case when electricity passes through a liquid electrolyte. I will now explain how we can measure the mass of the carriers of electricity required to convey a

given charge of electricity through a rarefied gas. In this case the direct methods which are applicable to liquid electrolytes cannot be used; but there are other, if more indirect, methods by which we can solve the problem. The first case of conduction of electricity through gases we shall consider is that of the so-called cathode rays—those streamers from the negative electrode in a vacuum tube which produce the well-known green phosphorescence on the glass of the tube. These rays are now known to consist of negatively electrified particles moving with great rapidity. Let us see how we can determine the electric charge carried by a given mass of these particles. We can do this by measuring the effect of electric and magnetic forces on the particles. If these are charged with electricity they ought to be deflected when they are acted on by an electric force. It was some time, however, before such a deflection was observed, and many attempts to obtain this deflection were unsuccessful. The want of success was due to the fact that the rapidly moving electrified particles which constitute the cathode rays make the gas through which they pass a conductor of electricity; the particles are thus, as it were, moving inside conducting tubes which screen them off from an external electric field; by reducing the pressure of the gas inside the tube to such an extent that there was very little gas left to conduct, I was able to get rid of this screening effect and obtain the deflection of the rays by an electrostatic field. The cathode rays are also deflected by a magnet; the force exerted on them by the magnetic field is at right angles to the magnetic force, at right angles also to the velocity of the particle, and equal to  $Hev \sin \theta$ , where  $H$  is the magnetic force,  $e$  the charge on the particle and  $\theta$  the angle between  $H$  and  $v$ . Sir George Stokes showed long ago that, if the magnetic force was at right angles to the velocity of the particle, the latter would describe a circle whose radius is  $\frac{mv}{eH}$  (if  $m$  is the mass of the

particle); we can measure the radius of this circle, and thus find  $\frac{m}{ve}$ .

To find  $v$ , let an electric force  $F$  and a magnetic force  $H$  act simultaneously on the particle, the electric and magnetic forces being both at right angles to the path of the particle and also at right angles to each other. Let us adjust these forces so that the effect of the electric force which is equal to  $Fe$  just balances that of the magnetic force which is equal to  $Hev$ . When this is the case  $Fe = Hev$ , or  $v = \frac{F}{H}$ . We can thus find  $v$ , and, knowing from the previous experiment

the value of  $\frac{m}{e}$ , we deduce the value of  $\frac{m}{e}$ . The value of  $\frac{m}{e}$  found in this way was about  $10^{-7}$ , and other methods used by Wiechert, Kaufmann and Lenard have given results not greatly different. Since  $m = 10^{-7}$ , we see that to carry unit charge of electricity by the

particles forming the cathode rays only requires a mass of these particles amounting to one ten-thousandth of a milligram, while to carry the same charge by hydrogen atoms would require a mass of one-tenth of a milligram.\*

Thus, to carry a given charge of electricity by hydrogen atoms requires a mass a thousand times greater than to carry it by the negatively electrified particles which constitute the cathode rays; and it is very significant that, while the mass of atoms required to carry a given charge through a liquid electrolyte depends upon the kind of atom—being, for example, eight times greater for oxygen than for hydrogen atoms—the mass of cathode ray particles required to carry a given charge is quite independent of the gas through which the rays travel and of the nature of the electrode from which they start.

The exceedingly small mass of these particles for a given charge compared with that of the hydrogen atoms might be due either to the mass of each of these particles being very small compared with that of a hydrogen atom or *else to the charge carried by each particle being large compared with that carried by the atom of hydrogen*. It is therefore essential that we should determine the electric charge carried by one of these particles. The problem is as follows: Suppose in an enclosed space we have a number of electrified particles each carrying the same charge, it is required to find the charge on each particle. It is easy by electrical methods to determine the total quantity of electricity on the collection of particles, and, knowing this, we can find the charge on each particle if we can count the number of particles. To count these particles the first step is to make them visible. We can do this by availing ourselves of a discovery made by C. T. R. Wilson working in the Cavendish Laboratory. Wilson has shown that, when positively and negatively electrified particles are present in moist dust-free air, a cloud is produced when the air is closed by a sudden expansion, though this amount of expansion would be quite insufficient to produce condensation when no electrified particles are present: the water condenses round the electrified particles, and, if these are not too numerous, each particle becomes the nucleus of a little drop of water. Now Sir George Stokes has shown how we can calculate the rate at which a drop of water falls through air if we know the size of the drop, and conversely we can determine the size of the drop by measuring the rate at which it falls through the air; hence, by measuring the speed with which the cloud falls, we can determine the volume of each little drop; the whole volume of water

\* Professor Schuster in 1889 was the first to apply the method of the magnetic deflection of the discharge to get a determination of the value of  $\frac{m}{e}$ ; he found rather widely separated limiting values for this quantity, and came to the conclusion that it was of the same order as in electrolytic solutions; the result of the method mentioned above, as well as those of Wiechert, Kaufmann and Lenard, make it very much smaller.



deposited by cooling the air can easily be calculated, and, dividing the whole volume of water by the volume of one of the drops, we get the number of drops, and hence the number of the electrified particles. We saw, however, that if we knew the number of particles we could get the electric charge on each particle; proceeding in this way I found that the charge carried by each particle was about  $6.5 \times 10^{-10}$  electrostatic units of electricity, or  $2.17 \times 10^{-20}$  electro-magnetic units. According to the kinetic theory of gases, there are  $2 \times 10^{19}$  molecules in a cubic centimetre of gas at atmospheric pressure and at the temperature  $0^\circ \text{C}$ .; as a cubic centimetre of hydrogen weighs about one-eleventh of a milligram, each molecule of hydrogen weighs about  $\frac{1}{(22 \times 10^{19})}$  milligrams, and each atom therefore about

$\frac{1}{(44 \times 10^{19})}$  milligrams, and as we have seen that in the electrolysis of solutions one-tenth of a milligram carries unit charge, the atom of hydrogen will carry a charge equal to  $\frac{10}{(44 \times 10^{19})} = 2.27 \times 10^{-20}$

electro-magnetic units. The charge on the particles in a gas, we have seen, is equal to  $2.17 \times 10^{-20}$  units. These numbers are so nearly equal that, considering the difficulties of the experiments, we may feel sure that the charge on one of these gaseous particles is the same as that on an atom of hydrogen in electrolysis. This result has been verified in a different way by Professor Townsend, who used a method by which he found, not the absolute value of the electric charge on a particle, but the ratio of this charge to the charge on an atom of hydrogen; and he found that the two charges were equal.

As the charges on the particle and the hydrogen atom are the same, the fact that the mass of these particles required to carry a given charge of electricity is only one-thousandth part of the mass of the hydrogen atoms shows that the mass of each of these particles is only about  $\frac{1}{1000}$  of that of a hydrogen atom. These particles occurred in the cathode rays inside a discharge tube, so that we have obtained from the matter inside such a tube particles having a much smaller mass than that of the atom of hydrogen, the smallest mass hitherto recognised. These negatively electrified particles, which I have called corpuscles, have the same electric charge and the same mass whatever be the nature of the gas inside the tube or whatever the nature of the electrodes; the charge and mass are invariable. They therefore form an invariable constituent of the atoms or molecules of all gases, and presumably of all liquids and solids.

Nor are the corpuscles confined to the somewhat inaccessible regions in which cathodic rays are found. I have found that they are given off by incandescent metals, by metals when illuminated by ultra-violet light, while the researches of Becquerel and Professor and Madame Curie have shown that they are given off by that wonderful substance the radio-active radium.

In fact, in every case in which the transport of negative electricity through gas at a low pressure (i.e., when the corpuscles have nothing to stick to) has been examined, it has been found that the carriers of the negative electricity are these corpuscles of invariable mass.

A very different state of things holds for the positive electricity. The masses of the carriers of positive electricity have been determined for the positive electrification in vacuum tubes by Wien and by Ewers, while I have measured the same thing for the positive electrification produced in a gas by an incandescent wire. The results of these experiments show a remarkable difference between the property of positive and negative electrification, for the positive electricity, instead of being associated with a constant mass  $\frac{1}{1000}$  of that of the hydrogen atom, is found to be always connected with a mass which is of the same order as that of an ordinary molecule, and which, moreover, varies with the nature of the gas in which the electrification is found.

These two results, the invariability and smallness of the mass of the carriers of negative electricity, and the variability and comparatively large mass of the carriers of positive electricity, seem to me to point unmistakably to a very definite conception as to the nature of electricity. Do they not obviously suggest that negative electricity consists of these corpuscles, or, to put it the other way, that these corpuscles are negative electricity, and that positive electrification consists in the absence of these corpuscles from ordinary atoms? Thus this point of view approximates very closely to the old one-fluid theory of Franklin; on that theory electricity was regarded as a fluid, and changes in the state of electrification were regarded as due to the transport of this fluid from one place to another. If we regard Franklin's electric fluid as a collection of negatively electrified corpuscles, the old one-fluid theory will, in many respects, express the results of the new. We have seen that we know a good deal about the "electric fluid"; we know that it is molecular, or rather corpuscular in character; we know the mass of each of these corpuscles and the charge of electricity carried by it; we have seen, too, that the velocity with which the corpuscles move can be determined without difficulty. In fact, the electric fluid is much more amenable to experiment than an ordinary gas, and the details of its structure are more easily determined.

Negative electricity (i.e., the electric fluid) has mass; a body negatively electrified has a greater mass than the same body in the neutral state; positive electrification, on the other hand, since it involves the absence of corpuscles, is accompanied by a diminution in mass.

An interesting question arises as to the nature of the mass of these corpuscles, which we may illustrate in the following way. When a charged corpuscle is moving, it produces in the region around it a magnetic field whose strength is proportional to the velocity of the corpuscle; now in a magnetic field there is an amount of energy pro-

portional to the square of the strength, and thus, in this case, proportional to the square of the velocity of the corpuscle.

Then, if  $e$  is the electric charge on the corpuscle and  $v$  its velocity there will be in the region round the corpuscle an amount of energy equal to  $\frac{1}{2} \beta e^2 v^2$  where  $\beta$  is a constant which depends upon the shape and size of the corpuscle. Again, if  $m$  is the mass of the corpuscle its kinetic energy is  $\frac{1}{2} m v^2$ , and thus the total energy due to the moving electrified corpuscle is  $\frac{1}{2} (m + \beta e^2) v^2$ , so that, for the same velocity, it has the same kinetic energy as a non-electrified body whose mass is greater than that of the electrified body by  $\beta e^2$ . Thus a charged body possesses, in virtue of its charge, as I showed twenty years ago, an apparent mass apart from that arising from the ordinary matter in the body. In the case of these corpuscles, part of their mass is undoubtedly due to the electrification, and the question arises whether or not the whole of their mass can be accounted for in this way. I have recently made some experiments which were intended to test this point; the principle underlying these experiments being as follows: if the mass of the corpuscle is the ordinary "mechanical" mass, then, if a rapidly moving corpuscle be brought to rest by colliding with a solid obstacle, its kinetic energy being resident in the corpuscle will be spent in heating up the molecules of the obstacle in the neighbourhood of the place of collision, and we should expect the mechanical equivalent of the heat produced in the obstacle to be equal to the kinetic energy of the corpuscle. If, on the other hand, the mass of the corpuscle is "electrical," then the kinetic energy is not in the corpuscle itself, but in the medium around it, and, when the corpuscle is stopped the energy travels outwards into space as a pulse confined to a thin shell travelling with the velocity of light. I suggested some time ago that this pulse forms the Röntgen rays which are produced when the corpuscles strike against an obstacle. On this view, the first effect of the collision is to produce Röntgen rays, and thus, unless the obstacle against which the corpuscle strikes absorbs all these rays, the energy of the heat developed in the obstacle will be less than the energy of the corpuscle. Thus, on the view that the mass of the corpuscle is wholly or mainly electrical in its origin, we should expect the heating effect to be smaller when the corpuscles strike against a target permeable by the Röntgen rays given out by the tube in which the corpuscles are produced, than when they strike against a target opaque to those rays. I have tested the heating effects produced in permeable and opaque targets, but have never been able to get evidence of any considerable difference between the two cases. The differences actually observed were small compared with the total effect, and were sometimes in one direction and sometimes in the opposite. The experiments, therefore, tell against the view that the whole of the mass of a corpuscle is due to its electrical charge. The idea that mass in general is electrical in its origin is a fascinating one, although it has not at present been reconciled with the results of experience.

The smallness of these particles marks them out as likely to

afford a very valuable means for investigating the details of molecular structure—a structure so fine that even waves of light are on far too large a scale to be suitable for its investigation, as a single wavelength extends over a large number of molecules. This anticipation has been fully realised by Lenard's experiments on the obstruction offered to the passage of these corpuscles through different substances. Lenard found that this obstruction depended only upon the density of the substance, and not upon its chemical composition or physical state. He found that, if he took plates of different substances of equal areas and of such thicknesses that the masses of all the plates were the same, then, no matter of what the plates were made, whether of insulators or conductors, whether of gases, liquids or solids, the resistance they offered to the passage of the corpuscles through them was the same. Now this is exactly what would happen if the atoms of the chemical elements were aggregations of a large number of equal particles of equal mass: the mass of an atom being proportional to the number of these particles contained in it, and the atom being a collection of such particles through the interstices between which the corpuscle might find its way. Thus, a collision between a corpuscle and an atom would not be so much a collision between the corpuscle and the atom as a whole, as between a corpuscle and the individual particles of which the atom consists; and the number of collisions the corpuscle would make, and therefore the resistance it would experience, would be the same if the number of particles in unit volume were the same, whatever the nature of the atoms might be into which these particles are aggregated. The number of particles in unit volume is, however, fixed by the density of the substance, and on this view the density (and the density alone) should fix the resistance offered by the substance to the motion of a corpuscle through it; this, however, is precisely Lenard's result, which is a strong confirmation of the view that the atoms of the elementary substances are made up of simpler parts, all of which are alike. This and similar views of the constitution of matter have often been advocated; thus in one form of it, known as Prout's hypothesis, all the elements were supposed to be compounds of hydrogen. We know, however, that the mass of the primordial atom must be much less than that of hydrogen. Sir Norman Lockyer has advocated the composite view of the nature of the elements on spectroscopic grounds, but the view has never been more boldly stated than it was long ago by Newton, who says:

"The smallest particles of matter may cohere by the strongest attraction and compose bigger particles of weaker virtue, and many of these may cohere and compose bigger particles whose virtue is still weaker, and so on for divers successions, until the progression ends in the biggest particles on which the operations in chemistry and the colours of natural bodies depend, and which by adhering compose bodies of a sensible magnitude."

The reasoning we used to prove that the resistance to the motion of the corpuscle depends only upon the density is only valid when

the sphere of action of one of the particles on a corpuscle does not extend as far as the nearest particle. We shall show later on, that the sphere of action of a particle on a corpuscle depends upon the velocity of the corpuscle—the smaller the velocity the greater being the sphere of action—and that, if the velocity of the corpuscle falls as low as  $10^7$  centimetres per second, then, from what we know of the charge on the corpuscle and the size of molecules, the sphere of action of the particle might be expected to extend further than the distance between two particles; and thus, for corpuscles moving with this and smaller velocities, we should not expect the density law to hold.

*Existence of Free Corpuscles or Negative Electricity in Metals.*

In the cases hitherto described the negatively electrified corpuscles had been obtained by processes which require the bodies from which the corpuscles are liberated to be subjected to somewhat exceptional treatment. Thus, in the case of the cathode rays the corpuscles were obtained by means of intense electric fields: in the case of the incandescent wire by great heat, in the case of the cold metal surface by exposing this surface to light. The question arises whether there is not to some extent, even in matter in the ordinary state and free from the action of such agencies, a spontaneous liberation of those corpuscles—a kind of dissociation of the neutral molecules of the substance into positively and negatively electrified parts, of which the latter are the negatively electrified corpuscles.

Let us consider the consequences of some such effect occurring in a metal, the atoms of the metal splitting up into negatively electrified corpuscles and positively electrified atoms, and these again after a time re-combining to form a neutral system. When things have got into a steady state, the number of corpuscles re-combining in a given time will be equal to the number liberated in the same time. There will thus be diffused through the metal swarms of these corpuscles: these will be moving about in all directions like the molecules of a gas, and, as they can gain or lose energy by colliding with the molecule of the metal, we should expect by the kinetic theory of gases that they will acquire such an average velocity that the mean kinetic energy of a corpuscle moving about in the metal is equal to that possessed by a molecule of a gas at the temperature of the metal; this would make the average value of the corpuscles at  $0^\circ$  C. about  $10^7$  centimetres per second. This swarm of negatively electrified corpuscles when exposed to an electric force will be sent drifting along in the direction opposite to the force; this drifting of the corpuscles will be an electric current, so that we could in this way explain the electrical conductivity of metals.

The amount of electricity carried across unit area under a given electric force will depend upon and increase with (1) the number of free corpuscles per unit volume of the metal; (2) the freedom with which these can move under the force between the atoms of the

metal; the latter will depend upon the average velocity of these corpuscles, for if they are moving with very great rapidity the electric force will have very little time to act before the corpuscle collides with an atom, and the effect produced by the electric force annulled. Thus, the average velocity of drift imparted to the corpuscles by the electric field will diminish as the average velocity of translation, which is fixed by the temperature, increases. As the average velocity of translation increases with the temperature, the corpuscles will move more freely under the action of an electric force at low temperatures than at high, and thus from this cause the electrical conductivity of metals would increase as the temperature diminishes. In a paper presented to the International Congress of Physics at Paris in the autumn of last year, I described a method by which the number of corpuscles per unit volume and the velocity with which they moved under an electric force can be determined. Applying this method to the case of bismuth, it appears that at the temperature of  $20^{\circ}$  C. there are about as many corpuscles in a cubic centimetre as there are molecules in the same volume of a gas at the same temperature and at a pressure of about a quarter of an atmosphere, and that the corpuscles under an electric field of 1 volt per centimetre would travel at the rate of about 70 metres per second. Bismuth is at present the only metal for which the data necessary for the application of this method exist; but experiments are in progress at the Cavendish Laboratory which it is hoped will furnish the means for applying the method to other metals. We know enough, however, to be sure that the corpuscles in good conductors, such as gold, silver or copper, must be much more numerous than in bismuth, and that the corpuscular pressure in these metals must amount to many atmospheres. These corpuscles increase the specific heat of a metal, and the specific heat gives a superior limit to the number of them in the metal.

An interesting application of this theory is to the conduction of electricity through thin films of metal. Longden has recently shown that when the thickness of the film falls below a certain value, the specific resistance of the film increases rapidly as the thickness of the film diminishes. This result is readily explained by this theory of metallic conduction, for when the film gets so thin that its thickness is comparable with the mean free path of a corpuscle, the number of collisions made by a corpuscle in a film will be greater than in the metal in bulk, thus the mobility of the particles in the film will be less and the electrical resistance consequently greater.

The corpuscles disseminated through the metal will do more than carry the electric current, they will also carry heat from one part to another of an unequally heated piece of metal. For if the corpuscles in one part of the metal have more kinetic energy than those in another, then, in consequence of the collisions of the corpuscles with each other and with the atoms, the kinetic energy will tend to pass from those places where it is greater to those where it is less, and in this way heat will flow from the hot to the cold parts of the metal; as

the rate with which the heat is carried will increase with the number of corpuscles and with their mobility, it will be influenced by the same circumstances as the conduction of electricity, so that good conductors of electricity should also be good conductors of heat. If we calculate the ratio of the thermal to the electric conductivity on the assumption that the whole of the heat is carried by the corpuscles, we obtain a value which is of the same order as that found by experiment.

Weber many years ago suggested that the electrical conductivity of metals was due to the motion through them of positively and negatively electrified particles, and this view has recently been greatly extended and developed by Riecke and by Drude. The objection to any electrolytic view of the conduction through metals is that, as in electrolysis, the transport of electricity involves the transport of matter, and no evidence of this has been detected; this objection does not apply to the theory sketched above, as on this view it is the corpuscles which carry the current; these are not atoms of the metal, but very much smaller bodies which are the same for all metals.

It may be asked, if the corpuscles are disseminated through the metal and moving about in it with an average velocity of about  $10^7$  centimetres per second, how is it that some of them do not escape from the metal into the surrounding air? We must remember, however, that these negatively electrified corpuscles are attracted by the positively electrified atoms and in all probability by the neutral atoms as well, so that to escape from these attractions and get free a corpuscle would have to possess a definite amount of energy: if a corpuscle had less energy than this then, even though projected away from the metal, it would fall back into it after travelling a short distance. When the metal is at a high temperature, as in the case of the incandescent wire, or when it is illuminated by ultra-violet light, some of the corpuscles acquire sufficient energy to escape from the metal and produce electrification in the surrounding gas. We might expect too that, if we could charge a metal so highly with negative electricity, that the work done by the electric field on the corpuscle in a distance not greater than the sphere of action of the atoms on the corpuscles was greater than the energy required for a corpuscle to escape, then the corpuscles would escape and negative electricity stream from the metal. In this case the discharge could be effected without the participation of the gas surrounding the metal and might even take place in an absolute vacuum, if we could produce such a thing. We have as yet no evidence of this kind of discharge, unless indeed some of the interesting results recently obtained by Earhart with very short sparks should be indications of an effect of this kind.

A very interesting case of the spontaneous emission of corpuscles is that of the radio-active substance radium discovered by M. and Madame Curie. Radium gives out negatively electrified corpuscles which are deflected by a magnet. Becquerel has determined the ratio of the mass to the charge of the radium corpuscles, and finds it is the same as for the corpuscles in the cathode rays. The velocity of the

radium corpuscles is, however, greater than any that has hitherto been observed for either cathode or Lenard rays: being, as Becquerel found, as much as  $2 \times 10^{10}$  centimetres per second, or two-thirds the velocity of light. This enormous velocity explains why the corpuscles from radium are so very much more penetrating than the corpuscles from cathode or Lenard rays; the difference in this respect is very striking, for while the latter can only penetrate solids when they are beaten out into the thinnest films, the corpuscles from radium have been found by Curie to be able to penetrate a piece of glass 3 millimetres thick. To see how an increase in the velocity can increase the penetrating power, let us take as an illustration of a collision between the corpuscle and the particles of the metal the case of a charged corpuscle moving past an electrified body; a collision may be said to occur between these when the corpuscle comes so close to the charged body that its direction of motion after passing the body differs appreciably from that with which it started. A simple calculation shows that the deflection of the corpuscle will only be considerable when the kinetic energy with which the corpuscle starts on its journey towards the charged body is not large compared with the work done by the electric forces on the corpuscle in its journey to the shortest distance from the charged body. If  $d$  is the shortest distance,  $e$  and  $e'$  the charge of the body and corpuscles, the work done is  $\frac{ee'}{d}$ ; while if  $m$  is the mass and  $v$  the velocity with which the corpuscle starts, the kinetic energy to begin with is  $\frac{1}{2}mv^2$ ; thus a considerable deflection of the corpuscle, i.e. a collision will occur only when  $\frac{ee'}{d}$  is comparable with  $\frac{1}{2}mv^2$ ; and  $d$ , the distance at which a collision occurs, will vary inversely as  $v^2$ . As  $d$  is the radius of the sphere of action for collision, and as the number of collisions is proportional to the area of a section of this sphere, the number of collisions is proportional to  $d^2$ , and therefore varies inversely as  $v^4$ . This illustration explains how rapidly the number of collisions and therefore the resistance offered to the motion of the corpuscles through matter diminishes as the velocity of the corpuscles increases, so that we can understand why the rapidly moving corpuscles from radium are able to penetrate substances which are nearly impermeable to the more slowly moving corpuscles from cathode and Lenard rays.

### *Cosmical Effects produced by Corpuscles.*

As a very hot metal emits these corpuscles it does not seem an improbable hypothesis that they are emitted by that very hot body, the sun. Some of the consequences of this hypothesis have been developed by Paulsen, Birkeland and Arrhenius, who have developed a theory of the Aurora Borealis from this point of view. Let us suppose that the sun gives out corpuscles which travel out through interplanetary space; some of these will strike the upper regions of the



earth's atmosphere and will then or even before then, come under the influence of the earth's magnetic field. The corpuscles when in such a field, will describe spirals round the lines of magnetic force; as the radii of these spirals will be small compared with the height of the atmosphere, we may for our present purpose suppose that they travel along the lines of the earth's magnetic force. Thus the corpuscles which strike the earth's atmosphere near the equatorial regions where the lines of magnetic force are horizontal will travel horizontally, and will remain at the top of the atmosphere, where the density is so small that but little luminosity is caused by the passage of the corpuscles through the gas; as the corpuscles travel into higher latitudes where the lines of magnetic force dip, they follow these lines and descend into lower and denser parts of the atmosphere, where they produce luminosity, which on this view is the Aurora.

As Arrhenius has pointed out, the intensity of the Aurora ought to be a maximum at some latitude intermediate between the pole and the equator, for, though in the equatorial regions the rain of corpuscles from the sun is greatest, the earth's magnetic force keeps these in such highly rarefied gas that they produce but little luminosity, while at the pole, where the magnetic force would pull them straight down into the denser air, there are not nearly so many corpuscles; the maximum luminosity will therefore be somewhere between these places. Arrhenius has worked out this theory of the Aurora very completely, and has shown that it affords a very satisfactory explanation of the periodic variations to which it is subject.

As a gas becomes a conductor of electricity when corpuscles pass through it, the upper regions of the air will conduct, and when air currents occur in these regions, conducting matter will be driven across the lines of force due to the earth's magnetic field, electric currents will be induced in the air, and the magnetic force due to these currents will produce variations in the earth's magnetic field. Balfour Stewart suggested long ago that the variation in the earth's magnetic field was caused by currents in the upper regions of the atmosphere; and Schuster has shown, by the application of Gauss' method, that the seat of these variations is above the surface of the earth.

The negative charge in the earth's atmosphere will not increase indefinitely in consequence of the stream of negatively electrified corpuscles coming into it from the sun, for as soon as it gets negatively electrified it begins to repel negatively electrified corpuscles from the ionised gas in the upper regions of the air, and a state of equilibrium will be reached when the earth has such a negative charge that the corpuscles driven by it from the upper regions of the atmosphere are equal in number to those reaching the earth from the sun. Thus, on this view, interplanetary space is thronged with corpuscular traffic, rapidly moving corpuscles coming out from the sun while more slowly moving ones stream into it.

In the case of a planet which, like the moon, has no atmosphere,

there will be no gas for the corpuscles to ionise, and the negative electrification will increase until it is so intense that the repulsion exerted by it on the corpuscles is great enough to prevent them from reaching the surface of the planet.

Arrhenius has suggested that the luminosity of nebulae may not be due to high temperature, but that the luminosity is produced by the passage through their outer regions of the corpuscles wandering about in space, the gas in the nebulae being quite cold. This view seems in some respects to have advantages over that which supposes the nebulae to be at very high temperatures. These and other illustrations, which might be given did time permit, seem to render it probable that these corpuscles may play an important part in cosmical as well as in terrestrial physics.

[J. J. T.]

Friday, May 10, 1901.

GEORGE MATTHEY, Esq., F.R.S., Vice-President,  
in the Chair.

PROFESSOR JAGADIS CHUNDER BOSE, M.A. D.Sc., Professor of  
Presidency College, Calcutta.

*The Response of Inorganic Matter to Mechanical and  
Electrical Stimulus.*

WHEN we pinch a living muscle, or send through it an electric shock, certain changes take place. A responsive twitch is produced; the muscle is changed in form, becoming shorter and broader; the particles of the living substance are strained under the stimulus. The effect of the shock then disappears, and the muscle is seen to relax into its usual form.

*Mechanical  
Response.*

This sudden change of form then, is one, but not the only, mode of response of a living substance to external stimulus. Under the stress the muscle is thrown into a state of distortion or strain. On the cessation of stimulus it automatically recovers. As long as it is alive, so long will it respond and recover, being ready again for new response. This brief disturbance of a living poise, to be immediately restored to equilibrium of itself, is quite unlike the rolling of a stone downhill from a push. For the stone cannot regain its original position, but the living tissue at once reasserts its first stable poise on the cessation of stress. Thus a muscle, as long as it is alive, remains ever-responsive. It is in intimate relation with the forces by which it is surrounded, always responding to, and recovering from, the multitudinous disturbances of its physical environment.

The living body is thus affected by external stimuli—mechanical shock, sound, electrical stimulus, and the stimuli of heat and light—which evoke in it corresponding responses.

In the case of the contraction of muscle by mechanical or electric shock, the effect is very quick, and the contraction and relaxation take place in too short a time for detailed observation by ordinary means. Physiologists, therefore, use a contrivance by which the whole process may be recorded automatically. This consists of a

lever arrangement, by which the contracting muscle writes down the history of its change, and recovery from that change. The record may be made on a travelling band of paper, which is moving at a uniform rate (Fig. 1). This autographic record gives us the most accurate information as to the characteristic properties and condition of the muscle. It gives us, too, its history and all its peculiarities.

*Characteristics  
of the Response  
Curve:*

- (1) *Amplitude,*
- (2) *Period,*
- (3) *Form.*

Just as one wave of sound is distinguished from another by its amplitude, period, and form, so are the curves of different muscles distinguished. For example, the period of tortoise muscle may be as large as several seconds, whereas the period for the wing of an insect is as small as  $\frac{1}{300}$ th of a second. In the same muscle, again, the form of the curve may undergo changes from fatigue, or from the effects of various kinds and quantities of drugs. In the autographic record of the progressive death of a muscle, the writing is bold and vigorous at first, but grows lethargic on the approach of death. In some strange way the molecules lose their mobility, rigidity supervenes, and the record of the dying muscle comes to an end. We may thus find out the effects of various external influences by studying the changes of form of the muscle curve.

We may stimulate the living substance in various ways — by light, *Electrical*, or by thermal, *Mechanical*, chemical, electrical, or mechanical stimuli. Of these, the electric means of stimulation is the most convenient, whereas the mechanical gives rise to the fewest complications. With regard to this response of living substances, the most important matters of study are the responses to single stimulus and to rapidly-succeeding stimuli, and the modification of response by fatigue and drugs.

A single shock causes a twitch, but the muscle soon recovers its original shape. The rising portion of the curve is due to contrac-

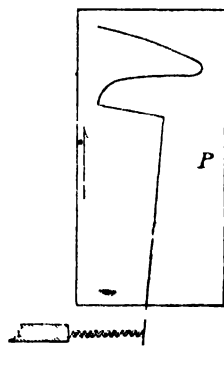


FIG. 1.—Mechanical Lever Recorder. The muscle *M* with the attached bone is securely held at one end, the other end being connected with the writing lever. Under the action of stimulus the contracting muscle pulls the lever and moves the tracing point to the right over the travelling recording surface *P*. When the muscle recovers from contraction, the tracing point returns to its original position. See on *P* the record of muscle curve.

tion, whereas the falling portions exhibit recovery (see curve in Fig. 1).

*Incomplete  
Tetanus.*

If, instead of a single stimulus, a succession of stimuli be superposed, the frequency of individual contractions also increases; the muscle has not time to recover; we get a jagged curve (*a*<sup>1</sup>, Fig. 11). But when the frequency is sufficiently increased, the intermittent effects are fused, and we get an almost unbroken curve. When the muscle attains its maximum contraction (corresponding to the

*Complete  
Tetanus.*

frequency and strength of stimulus), it appears to be held rigid, and recovers only on the cessation of stimulus (*b*<sup>1</sup>, Fig. 11).

*Fatigue.*

When the muscle is continuously excited it grows fatigued. The height of the curve grows continuously less. This is seen in a series of single twitches (Fig. 4). It is also seen in tetanus, where there is a decline of the upper portion of the curve.

*Influence  
of Drugs.*

Drugs may act as stimulants, or produce depression, according to their nature. As extreme cases of such depressing agents we may instance poisons, which kill the response of living tissue. All signs of sensibility then disappear.

*Other Modes  
of Expression  
of Living  
Response.*

This mechanical method of studying the response of living substances is, however, very limited in its application. For example, when a piece of nerve is stimulated, there is no visible change of form. When light falls on the retina there is no change of form, but it responds by transmitting to the brain a visual impulse. What, then, is this visual impulse which is sent along the optic nerve, causing the sensation of light?

Thanks to the work of Hombgren, Dewar, McKendrick and others, it is possible to answer this question. If we excise an eye, say of a frog, and substitute a galvanometer in the visual circuit in the place of the perceiving brain, it is found that each time a flash of light falls on the eye there is produced an electric twitch—that is to say, there is a sudden production of current, which ceases on the cessation of light-stimulus. Stronger light produces stronger electric twitch in the galvanometer, just as it produces stronger sensation in the brain. The visual impulse thus appears to be the concomitant of an electric impulse. This conclusion is supported by the fact that a luminous sensation is occasioned (without the action of light), by simply sending an electric current to the brain through the optic nerve.

The visual circuit is therefore like an electric circuit. The retina is a potential voltaic element. The nerve is the conductor. The brain is the detector of current, or a very highly sensitive galvanometer. Unless these three elements are in good order, no light-message can be perceived. We must have the current-generator or retina, and

the conductor or optic nerve, free from injury. Finally, just as the galvanometer will fail to detect a current if its suspension-thread be broken by rough usage, so, after a violent blow, the brain will no longer perceive, though the terminal organ, the retina, and the connecting optic nerve may be intact.

So we see that stimulus evokes an electrical change also, in a living tissue. I shall now proceed to enter into some detail regarding this electric mode of response.

### *Hydraulic Model.*

The various complicated phenomena of electric response may perhaps be rendered more easily intelligible by means of a hydraulic model (*l*, Fig. 2). Imagine an indiarubber pipe full of water, whose two ends A and B are at the same level. There would then be no current in the side or canal-pipe P. But suppose the end A is struck, a wave of disturbance will travel from A towards B. At a given moment the level at the A end will be raised,

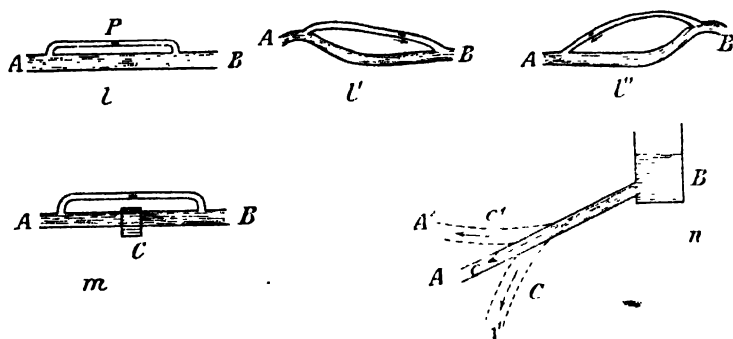


FIG. 2.—Hydraulic Models.

and the side tube will exhibit a current from A to B (*l'*, Fig. 2); but, after a little while, A will subside to the normal level, the disturbance having meanwhile travelled to B, whose level will now be raised. The current in the side tube will now be reversed in direction (*l''*, Fig. 2). A disturbing shock applied to one end of A B will thus produce a diphasic variation, and a float or indicator in the side pipe will exhibit this effect by alternate movement, first to one side and then to the other. If, however, the rate of transmission of disturbance be very great, then the indicator will fail to show any movement, inasmuch as it will be acted on by two equal and opposite impulses almost simultaneously.

1. To make the indicator exhibit the effect of shock in producing disturbance of level, we may proceed as follows. We may clamp the pipe in the middle at C (see *m*, Fig. 2), so that when one end is struck the disturbance may not proceed to the other end, the clamp

acting as a block. In such a case, when A is struck, the indicator will move to the right; when B is struck, it will move to the left. Thus we obtain effects which are reversible.

2. Or we may detect the effect of shock by the variations that it may produce in the intensity of the current. Take the case of *n*, Fig. 2, where there is a permanent difference of level between the two ends; one end, say B, being also more securely held, so that a shock produces less disturbance of level there than at A. As there is a permanent difference of level between B and A, there will be a current the normal intensity of which (*c*) will depend on the resting difference of level between B and A. If the pipe be now struck, A will be relatively more disturbed, and there may then be produced either a decrease ( $BA^2$ ) or an increase ( $BA^1$ ) of original difference of level. In the former case we shall have less current ( $c^1$ ), that is to say, the shock will have the effect of a *negative variation* of current; in the latter case there will be a greater flow (*C*) or a *positive variation*.

These models may help us in framing a mental image of that electrical variation which constitutes the response to stimulus of a living tissue.

If we take a piece of living muscle whose surface is uninjured, then any two points (A and B) on such surface being in a similar molecular condition, their electrical level or potential will be the same. They are *iso-electric*. No current will be exhibited by the indicating galvanometer when two non-polarisable electrodes\* con-

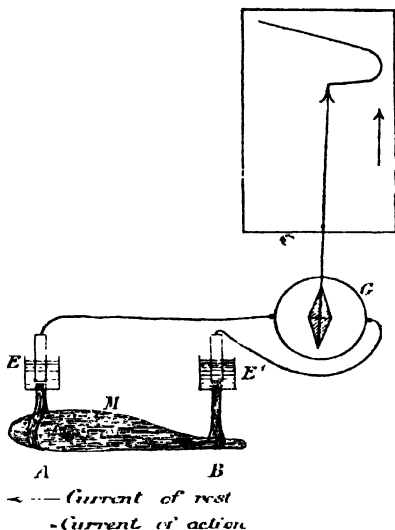


FIG. 3.—Magnetic Lever Recorder. *M* muscle; *A* uninjured, *B* injured ends. *EE'* non-polarising electrodes connecting *A* and *B* with galvanometer *G*. Stimulus produces "negative variation" of current of rest. Index connected with galvanometer needle records curve on travelling paper (in practice, moving galvanometer spot of light traces curve on photographic plate). Rising part of curve shows effect of stimulus; descending part, recovery.

\* Zinc rods in solution of  $ZnSO_4$ , with two dependent strips of cloth, moistened with  $NaCl$  solution passed round the muscle at A and B.

neoted with it are applied to A and B. But if one of the two points, say B, be injured by a cut, or burn, application of strong acids, or by alkalies, then, the conditions of A and B being different, there will be a difference of electric level or potential between them, and a current will flow from the injured to the uninjured, that is from B to A (Fig. 3). This current remains approximately constant as long as the muscle is at rest, and is for this reason known as "current of rest." As it is primarily due to injury, it is also known as "current of injury." If now the muscle be thrown into an excitatory state\* by stimulus, there will be a greater relative disturbance at the uninjured A, and the original difference of electric level will be disturbed. In this case we have an analogue to  $c'$  in  $n$ , Fig. 2, where the shock produced a decrease of original difference of level. There would thus be a *negative* variation or diminution of the original current of rest. This negative variation is sometimes called an "action current." The transitory electrical variation constitutes the "response." Its intensity measures the intensity of the stimulus.

But we saw in the hydraulic model the possibility of a positive variation or increase of current, by shock. This is also found to be the case in some types of living response. In the retina, the stimulus of light produces a positive variation. It will thus be seen that there are two kinds of response given by living substances: (1) the negative, instanced by muscle, and (2) the positive, shown by the retina. Again, the same tissue under different conditions may give rise to responses having opposite signs. Thus Dr. Waller finds that while fresh nerve gives negative, the stale nerve gives positive variation.†

We have here, then, a way of obtaining curves of response by electric means. After all it is not very different essentially from the mechanical method. In this case we use a magnetic lever, the needle of the galvanometer, which is deflected by the electric pull of the current, generated under the action of stimulus, just as the mechanical lever was deflected by the mechanical pull of the muscle contracting under stimulus (Fig. 3).

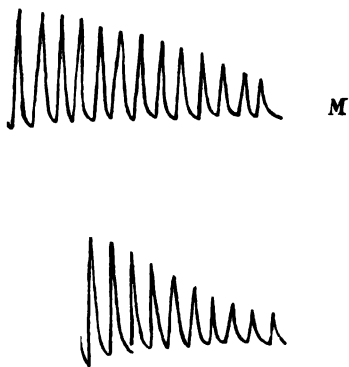


FIG. 4.—Simultaneous records of the (*M*) mechanical and (*E*) electrical response of gastrocnemius muscle of a frog. The muscle exhibits fatigue (Waller).

\* The excitatory reaction is, in the case of some living substances, of a more or less local character. In others, as nerves, it may be conducted to distant points.

† See Waller, 'Animal Electricity,' p. 61.



If a piece of muscle be taken, and simultaneous records of its response be made by the mechanical and electrical recorders, it will be found that the one is practically a duplicate of the other. This is well shown in a pair of records taken by Dr. Waller, and here reproduced (Fig. 4). It will be seen that the peculiarities of either curve are re-exhibited in the other. The muscle acted on grew fatigued, and both sets of response-curves show this effect by their gradual diminution of amplitude.\*

*Response  
in Plants.*

I find that the electric response seen in animal tissues is also strongly exhibited by the tissues of plants. For experimental illustration we may take the leaf-stalk of horse-chestnut.†

1. Let us take such a stalk, and securely tying two strips of moistened cloth to A and B to prevent shifting of contact, connect

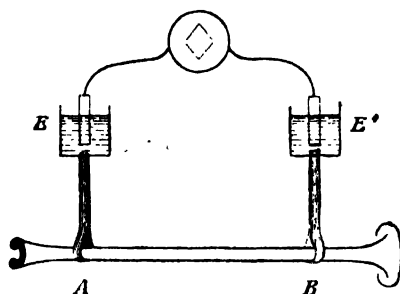


FIG. 5.—Response in plants. There being no block, effects at A and B are equal and opposite; hence no resultant effect.

these with two leading non-polarisable electrodes, E and E' (see Fig. 5). From what has been said before, it will be seen that these two points being practically iso-electric, little or no current will flow through the galvanometer. If, now, we apply a mechanical stimulus to the whole stalk either (1) by tapping or (2) by holding it at its two ends, and giving it a rapid torsional vibration, we shall have similar disturbances produced both at A and B, and there will be

practically no resultant current of response.

2. We may now use the block method (Fig. 6). That is to say, the stalk is held securely in the middle by a clamp C, so that a disturbance made at one end will not reach the other. The electric contact is made with the uninjured, therefore iso-electric, points A and B, by securely tying the stalk with strips of moistened cloth at those points, as in the experiment just described. If now the A half be subjected to taps, or to torsional vibration, there will be a current of response through the stalk from the excited to the unexcited end. If the B end be next excited, a current in the reverse direction will be observed, in this case also from the excited to the unexcited end (a, Fig. 6).

\* Waller, 'Animal Electricity,' p. 13.

† Various parts of plants—leaves, stems, stalks, and roots—will give electric response. In some there is rapid fatigue, whereas in others there is little fatigue. I intend to publish at a future date a more detailed account of these responses and their modifications by anæsthetics, poisons, and other agencies.

3. Or, taking again an unblocked stalk, let one contact be made in the usual manner at the end A, and the other at the end B, which is now injured by a cut (see Fig. 7). There will now be a permanent difference of electric level between the two ends, and a current of injury will be found to flow through the stalk from the injured to the uninjured. This contact at the injured end may be made in a very simple manner by passing a strip of moistened cloth through a slit in the stalk at B. Or, better still, instead of the cut

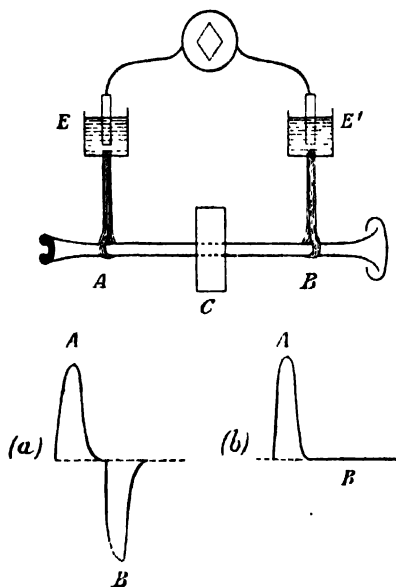


FIG. 6.—Response in plants by block method and response curves. C, clamp or block. Stimulation of A end produces current in one direction, that of B end in opposite direction, as shown by curves given in (a). In (b) is shown abolition of response in B half when killed.

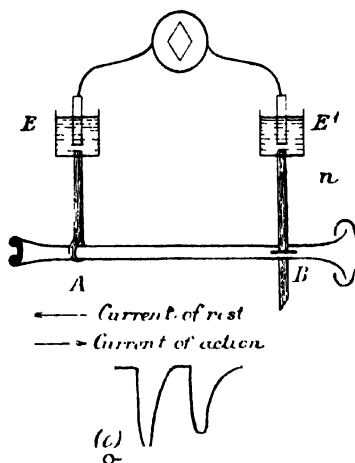


FIG. 7.—Response in plants—negative variation. There is a resting current owing to injury at B. Stimulation produces a diminution of this resting current, as shown in (c). The dotted line represents the galvanometer zero.

we may use a few drops of strong KHO solution, to injure the B end. If now the stalk be subjected to mechanical stimulus, it will be found that there is a responsive negative variation, or a diminution in the original current of rest (c, Fig. 7).

Thus we see that under stimulation the plant, like muscle or nerve, is thrown into an excitatory state of which the electrical change is the concomitant, this electric response being regarded by physiologists as proof of the living condition of the substance.

4. But how can we be certain that this electrical indication is peculiar, *sui generis*, to the physiological or living state? The crucial

test is supposed to lie in the modification of response under anæsthetics or poisons, when "that which is physiological, i.e. dependent on the physico-chemical conditions peculiar to the living state, will be suppressed; that which is purely physical will persist."\* In order, then, to determine whether response in plants is or is not of a physiological character, we may subject them to the action of chloroform. Taking a fresh stalk we get the usual strong response. We now apply chloroform, and find as anæsthetic action proceeds, that the responses wane, and are finally abolished. There are various other poisons which I find to be very effective in killing response.

5. The physiological nature of the response may be further demonstrated if we repeat experiment 2, after killing the stalk by brief immersion in hot water. No response current will now be evoked on stimulation of either A or B end.

As the conditions in 2 and 5 were exactly similar, except for the fact that in the former case the stalk was alive, and in the latter killed, on the method of difference we are justified in concluding that the response was physiological, or characteristic of a living state of matter.

6. Or we may demonstrate the same fact in a more striking manner by a modification of experiment 2. One half of the stalk, say the B half, is killed, by dipping that half in hot water. On now subjecting the B half to stimulation, there is no response; but stimulation of the A end gives strong response (b, Fig. 6).

*Universal  
Applicability  
of the test of  
Electric  
Response.*

Nothing has yet been said of the advantage of the electrical over the mechanical method of obtaining response. As has been said before, the mechanical method is limited in its application. A nerve, for example, does not undergo any change of form when excited, and its response cannot therefore be detected by this method. But by the electrical

method we are able to detect, not only the response of muscles, but that of all forms of living tissue.

The intensity of electrical response is also a measure of physiological activity. When this physiological activity of the living substance is diminished by anæsthetics, the electrical responses are also correspondingly diminished. And when the living tissue is in any way killed, the electrical response disappears altogether. Hence it is said that "the most general and the most delicate sign of life is the electrical response."†

Thus, electrical response is regarded as the criterion between the living and non-living. Where it is, life is said to be; where it is not found, we are in presence of death, or else of that which has never lived: for in this respect there is a great gulf fixed between the

\* Waller, 'Animal Electricity,' p. 104.

† "The Electrical Sign of Life. . . . An isolated muscle gives sign of life by contracting when stimulated. . . . An ordinary nerve, normally connected

organic living and the inorganic or non-living. The phenomena of the inorganic are dominated merely by physical forces, while on the other side of the chasm, in the domain of the living, inscrutable vital phenomena, of which electric response is the sign-manual, suddenly come into action.

But is it true that the inorganic are irresponsible? That forces evoke in them no answering thrill? Are their particles for ever locked in the rigid grasp of immobility? As regards response, is the chasm between the living and inorganic really impassable?

Thanks to the courtesy of the authorities of the Davy-Faraday Laboratory, I have been enabled to complete the investigations on this subject, commenced in India, under this very roof. I shall now proceed to submit the question before you to an experimental test.

*Inorganic  
Response.*

Taking a piece of tin wire, I arrange it in exactly the same way as the stalk of the horse-chestnut (see Figs. 6 and 8). That is to say, it is clamped in the middle, and secure electrolytic contacts are made, through non-polarisable electrodes, which lead to a galvanometer. If all strains have been completely removed, the two points, A and B, will be found iso-electric. If now I take the end A and strike it, or subject it to torsional vibration, you will observe that the galvanometer spot on the screen, hitherto quiescent, moves in one direction, showing the existence of the "current of action." I stop the disturbance, and you watch it creeping back to its original position, exhibiting a complete recovery. As long as the wire is excited, so long will the electric variation persist. Greater intensity of vibration will produce greater electric variation. Stimulation of the B end will produce a deflection in the opposite direction.

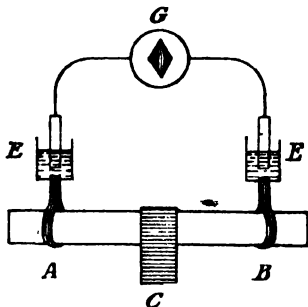


FIG. 8.—Experimental arrangement to show electric response in metallic wires. C, clamp.

Or, following experiment 8, we may demonstrate the fact of electric response by the method of injury. One end of the wire is touched with KHO, and the usual current of injury is observed. On now stimulating the wire, a diminution of this current of injury, or *negative variation*, will be produced.

with its terminal organs, gives sign of life by means of muscle, which by direct or reflex path is set in motion when the nerve-trunk is stimulated. But such nerve, separated from its natural termini, isolated from the rest of the organism, gives no sign of life when excited, either in the shape of chemical or of thermic changes, and it is only by means of an electrical change that we can ascertain whether or no it is alive. . . . The most general and most delicate sign of life is then the electrical response."—Waller, in 'Brain,' pp. 3 and 4, Spring 1900.

With tin wire under normal conditions, the current through the wire is always from the unexcited to the excited end, and from the excited to the unexcited through the galvanometer.\* But just as in living substances we find two opposite kinds of response (e.g. nerve giving negative and retina positive variation), so also the responses given by some inorganic substances are of opposite signs to that of tin. For example, silver sometimes, especially in cold weather, passes into a peculiar molecular condition in which it gives the reverse response to that of tin, the "action current" in the wire being from the excited to the unexcited. An interesting transition from one class to the other is sometimes found in the behaviour of lead. Under feeble stimulus the current is away from the stimulated, and under stronger, towards that end. The majority of metals, however, behave like tin.

This simple form of experiment with metallic wire has been devised for the special purpose of bringing the essential points out clearly. But it labours under certain defects. Unless carefully carried out, there may be shifting of contacts; there may be variations of resistance by the evaporation of the liquid contacts; and quantitative measurements also are rendered difficult, for want of some means of graduating the intensity of stimulus. I will now describe a perfect form of apparatus for exhibiting the electrical response of metallic wires to mechanical stimulus, in which all these difficulties have been completely overcome.

*Experimental  
Modifications.*

In the typical experiment (Fig. 8), instead of making the galvanometer connection through electrolytic contacts we may cut A B into two (b, Fig. 9), and place the galvanometer in the gap, connecting A B directly by electrolyte.

This leads to c, Fig. 9, where A and B are held parallel to each other in an electrolytic bath (water).† Mechanical vibration may now be applied to A without affecting B, and *vice versa*.

The actual apparatus, of which this is a diagrammatic representation, is seen in d, Fig. 9.

Two pieces, from the same specimen of wire, are clamped separately at their lower ends by means of ebonite screws, in an L-shaped piece of ebonite. The wires are fixed at their upper ends to two electrodes (leading to the galvanometer), and kept moderately and uniformly stretched by spiral springs. The handle, by which a torsional vibration is imparted to the wire, may be slipped over either electrode. The amplitude of vibration is measured by means of a graduated circle, not shown in the figure.

\* The galvanometer in the above arrangement is interposed, as it were, in the electrolytic part of a voltaic cell. The portion of tin wire under excitement becomes zincoid. I mention this, as some misunderstandings and wrong inferences have arisen from not distinguishing between the direction of the current in the electrolytic part and that in the rest of the circuit.

† In all the experiments hereafter described the electrolyte is water unless the contrary be stated.

It will be seen from these arrangements :

(1) That the cell depicted in *d*, Fig. 9, is essentially the same as that in Fig. 8.

(2) That as the wires in the cell are immersed to a definite depth in the electrolyte there is always a perfect and invariable contact between the wire and the electrolyte. The difficulty as regards variation of contact is thus eliminated.

(3) That as the wires A and B are clamped below, we may impart a sudden molecular disturbance to either A or B by giving a

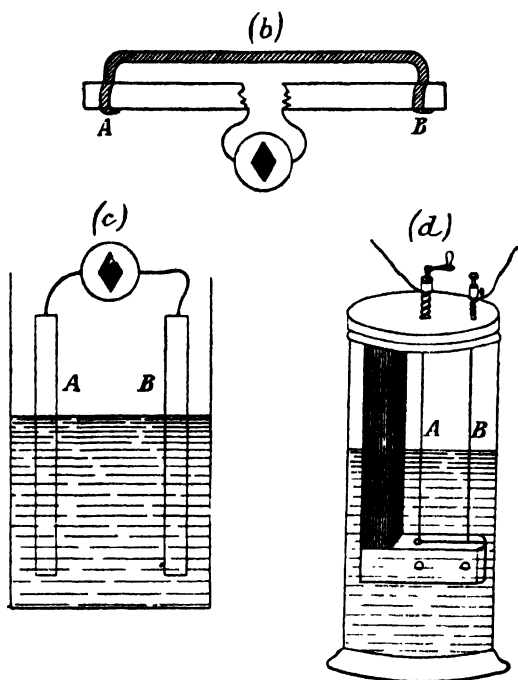


FIG. 9.—Modifications of experimental arrangement to show electric response in metals.

quick torsional vibration round the vertical wire, as axis, by means of the handle. As the wire A is separate from B, disturbance of one will not affect the other. Vibration of A produces a current in one direction, vibration of B in the opposite direction. Thus we have means of verifying every experiment by obtaining corroborative and reversal effects. When the two wires have been brought to exactly the same molecular condition by the processes of annealing or stretching, the effects obtained on subjecting A or B to any given stimulus are always equal.

But if, to begin with, the two were not in the same molecular condition, an initial P.D. would exist between them, and then, owing to the difference in the anodic and cathodic sensitiveness, the responses given by the two would not be identical.

Usually I interpose an external resistance varying from one to five megohms according to the sensitiveness of the wire. The resistance of the electrolyte in the cell is thus relatively small, and the galvanometer deflections are proportional to the E. M. variations. It is always advisable to have a high external resistance, as by this means one is not only able to keep the deflections within the scale, but one is not troubled by minute accidental disturbances.

When the cell is freshly made, the wires, owing to the strain set up during the mounting, may exhibit slightly erratic responses. Both should then be short-circuited, and after being subjected to vibrations for a time, the cell should be allowed a short period of rest. In this way, after a little practice, it is always possible to bring the response to a normal condition. The responses subsequently obtained become extraordinarily consistent. There is no reason why perfect results should not be arrived at, if these conditions are fulfilled.

*Application of Stimulus.* If now a rapid torsional vibration be given to A (or B), there will be induced an electromotive variation. The intensity of stimulus is increased with the amplitude of vibration. Greater intensity of response is always obtained with greater intensity of stimulus.

*Considerations showing that Electric Response is due to Molecular Disturbance.*—1. The electromotive variation varies with the substance. With superposition of stimuli, a relatively high value is obtained in tin, amounting sometimes to nearly half a volt, whereas in silver the electro-motive variation is only about .01 of this value. The intensity of the response, however, does not depend on the chemical activity of the substance, for the electromotive variation in the relatively chemically-inactive tin, and even gold, is greater than that of zinc. Again, the sign of response in silver, positive or negative, depends on its molecular condition.\*

2. It may be thought that the electro-motive variation is due to some thermo-electric effect, inasmuch as the wire may be heated by vibration. The heat produced by a single vibration, however, must be very small. In order to test whether heating of the wire would produce effects comparable in magnitude to that produced by vibration, I made a cell with lead wire (the external resistance interposed in the circuit was 100,000 ohms). On subjecting one wire to the heating action of concentrated light from an arc lamp, during a continuous exposure of one minute, the effect on the galvanometer was a deflection of barely one division of the scale. But when the same wire was subjected to five quickly succeeding vibrations, lasting altogether only a few seconds, there was produced the very large deflection of 180 divisions.

Numerous other effects will be described presently which cannot be explained on the thermo-electric theory of action. I find for instance that the

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\* It is curious to note that the response of silver filings to Hertzian waves also depends on the molecular condition of the silver. In one condition there is produced a diminution of resistance, or positive effect: in the other the resistance is increased, i.e. the effect shown is negative. (See my Paper on "Electric Touch," Proc. Roy. Soc., Aug. 1900.)

intensity of response is very much modified by the effect of varying doses of chemical reagents. For example, with a .25 per cent. strength of potash solution, the response was 57 divisions; but the increase of this strength to .75 and upwards completely abolished all response.

3. It may be urged that the electro-motive effect is due in some way to (1) the friction of the vibrating wire against the liquid, or (2) some unknown surface action at the point in the wire of the contact of liquid and air surfaces. It is, however, to be remembered as regards (1), that the amount of this friction is exceedingly small; the movement of the wire at the lower fixed end being zero, that at the upper end is through an angle of about  $180^\circ$ . (2) Variation of surface, similarly, must be almost non-existent under the arrangements adopted for experiment.

Both these questions may, however, be subjected to a definite and final test. When the wire to be acted on is clamped below, and torsional vibration is imparted to it, a strong molecular disturbance is produced. If now it be carefully released from the clamp, and the vibration repeated as before, there could be little molecular disturbance due to torsion of the wire, but the liquid friction and surface variation, if any, would remain. The effect of any slight disturbance outstanding owing to shaking of the wire would be relatively very small.

We can thus determine the effect of liquid friction and surface action by repeating experiments with and without clamping. In a tin wire cell (with interposed external resistance equal to 1,000,000 ohms), the wire A was subjected to a series of vibrations through  $180^\circ$ , and a deflection of 210 divisions was obtained. A corresponding negative deflection resulted on vibrating the wire B. Now A was released from the clamp, so that it could be rotated backward and forward in the water by means of the handle. On vibrating the wire A no measurable deflection was produced, thus showing that neither water friction nor surface variation had anything to do with the electric action. The vibration of the still clamped B gave rise to the normal strong deflection.

As all the rest of the circuit was kept absolutely the same in the two different sets of experiments, these results conclusively prove that the electro-motive variation is solely due to the molecular disturbance produced by mechanical vibration in the acted wire.

The question of surface action again can be finally disposed of if we take a cell (with external high resistance) and tilt it backwards and forwards. This will produce a great surface variation, yet little or no current will be detected. But vibration of the wire will produce the normal strong response.

The same strong response is obtained, further, when the air surface is completely abolished, vibration being communicated to a completely-immersed wire by means of an ebonite clip-holder.

A new and theoretically interesting molecular voltaic cell may thus be made, in which the two elements consist of the *same metal*. Molecular disturbance is in this case the source of energy. A cell once made may be kept in working order for a considerable time by pouring in a little vaseline to prevent evaporation of the liquid.

I shall now proceed to describe in detail the response curves obtained with metals, and as a substance which gives good results I shall take tin. The records given in this paper were obtained; some by following the galvanometer deflection with a pencil, others by direct photography, and have been exactly reproduced. The gal-



vanometer used was similar, as regards sensitiveness and the period of swing of the needle, to that employed for physiological records.

*Effects of  
Single Stimuli.*

Fig. 10, *a*, gives a series, each of which is the response curve for a single stimulus of uniform intensity (amplitude of vibration,  $180^\circ$ ). Observe the perfect similarity of all these curves, and their resemblance to the curves of response in living tissues (Fig. 10, *b*). The rising portion of the curve is somewhat steep, and the recovery convex to the abscissa, the fall being relatively rapid in its first, and less rapid in its latter, parts. As the electric variation is the concomitant effect of molecular disturbance—a temporary upset of molecular equilibrium,—on the cessation of the external stimulus the excitatory state and its expression in electric variation disappear, with the gradual return of the molecules to their condition of equilibrium, a process which is seen clearly in the curve of recovery.

Different metals exhibit different periods of recovery, and this

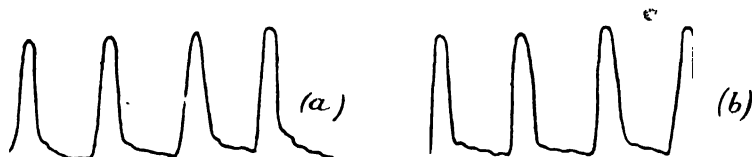


FIG. 10.—(*a*) Series of electric responses to successive mechanical stimuli at intervals of half a minute, in tin. (*b*) Mechanical responses in muscle.

again is modified by any influence which affects the molecular condition.

That the excitatory state persists for a time even on the cessation of stimulus can be independently shown by keeping the galvanometer circuit open during the application of stimulus, and completing it at various short intervals after the cessation, when a persisting electrical effect, diminishing rapidly with time, will be apparent.\*

We have already seen how similar the response-curves of the in-

\* Observe how similar the above is to the excitatory electrical effect due to stimulus, in living tissue, such as nerve. "The excitatory state evoked by stimulus manifests itself in nerve fibre by electromotive changes, and as far as our knowledge goes, by these only. . . . The conception of such an excitable living tissue as nerve implies that of a molecular state which is in stable equilibrium. This equilibrium can be readily upset by an external agency, the stimulus, but the term 'stable' expresses the fact that a change in any direction must be succeeded by one of opposite character, this being the return of living structure to its previous state. Thus the electric manifestation of the excitatory state is one whose duration depends upon the time during which the external agent is able to upset and retain in a new poise the living equilibrium, and if this is extremely brief, then the recoil of the tissue causes such manifestation to be itself of very short duration."—*Text-book of Physiology*, edited by Schäfer, p. 453.

organic are to those of the living substance. We have yet to see whether the similarity extends to this point only, or goes still further. Are the response-curves of the inorganic modified by the influence of external agencies, as the living responses were found to be? If so, are the modifications similar? I shall now place two sets of curves side by side, when it will become apparent whether or no similar external influences produce similar results in the two classes of phenomena.

*Effect of  
Superposition  
of Stimuli.*

It has been said that, with rapidly succeeding stimuli, when the intermittent effects of single shocks are fused, a tetanic condition is produced in a muscle, and we obtain an almost unbroken curve (see *b'*, Fig. 11). If the frequency is not sufficiently great, there is an incomplete tetanus, and the response-curve becomes jagged (see *a'*, Fig. 11).

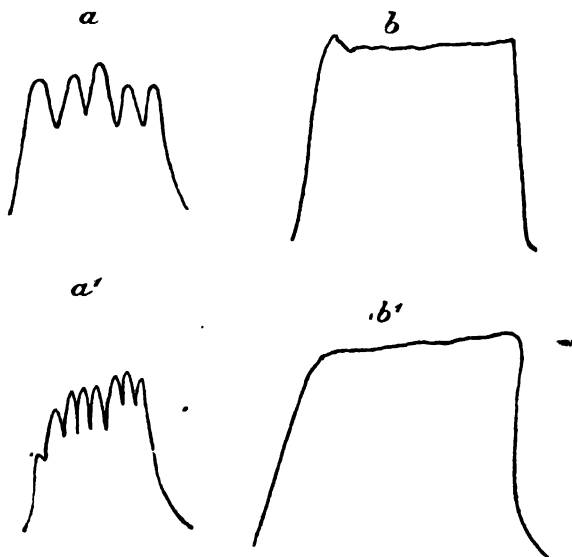


FIG. 11.—Effects analogous to (a) incomplete and (b) complete tetanus, in tin.  
(a') Incomplete and (b') complete tetanus in muscle.

The very same thing occurs in metals. I subject the wire to quickly succeeding vibrations. The curve rises to its maximum; further stimulation adds nothing to the effect, and the deflection is held, as it were, rigid, so long as the vibration is kept up. With lesser frequency of stimulus, we find an incomplete state of tetanus, and the curve becomes jagged (see *a* and *b*, Fig. 11).

It is also curious that the maximum effect is produced almost

invariably after a definite period of stimulation. In tin, at least, successive tetanic curves are almost exactly similar. The maximum effect depends on the intensity of the stimulus (Fig. 12).

*Fatigue.* Amongst living substances we find nerve practically indefatigable. Successive curves are exactly similar. But with muscle there is a rapid decline in the responses (Fig. 4). Fatigue, however, disappears

after a period of rest. It is generally supposed to be due to the working of two processes conjointly—the breakdown of force-producing material and the accumulation of “fatigue-stuffs.” It is thought that fatigue is removed by the action of the circulating blood in bringing in fresh material and carrying away fatigue products. But that this cannot furnish a complete explanation of the

phenomena is shown by the fact that excised bloodless muscle acted on by stimulus, recovers from fatigue after a short period of rest, though here there is no blood-supply to repair the damage and remove the waste products.

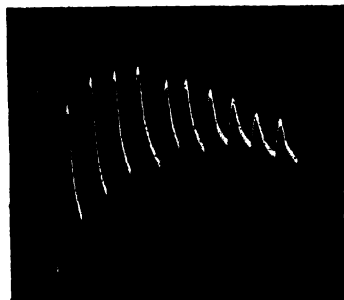


FIG. 13.—Photographic record of fatigue in tin (compare with Fig. 4).

primarily due to over-strain, and not to fatigue products, is seen from the fact that a brief period of repose hastens its removal in this case also.

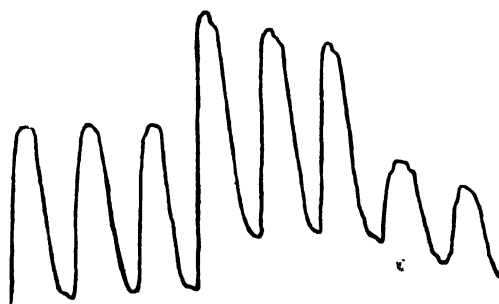


FIG. 12.—Tetanic curves in tin, showing effects of different intensities of stimuli. The three curves to the left show effect of vibration with amplitude of 90°; the next three are due to stronger intensity of stimulus, amplitude = 180°; the amplitude was now reduced to 90°, and the last two, owing to fatigue, show feeble response than the first three.

Turning to inorganic substances, we find different metals exhibiting fatigue. But tin exhibits very little, reminding us in this of the behaviour of nerves. Even here, however, after prolonged action, fatigue is sometimes observed. The fatigue curve here reproduced was obtained from tin that had been acted on for several days, and its remarkable similarity to the curve of fatigue in muscles

will be at once apparent (see Figs. 13 and 4). That fatigue is pri-

*Stimulus  
of Light.*

Perhaps before completing what I have to say on the modification of response by external agencies, it will be well to make some reference to the action of other forms of stimulus and other modes of detection of response. In this investigation I have used the mechanical form of stimulus as being the simplest and giving rise to the fewest complications. Time does not allow of my entering here upon the question of the action of electric stimulus in causing response. I have dealt with this subject in some detail elsewhere. I may, however, say a few words on the effect of light stimulus.

If one of the sensitised wires in the cell already described be subjected to light it will give an electric response, and under certain circumstances an oscillatory after-effect will be seen on the cessation of light. This latter fact may, perhaps, explain certain phenomena of visual recurrence to be noticed presently.

*Artificial  
Retina.*

The molecular strain produced by stimulus can not only be detected by the phenomena of electromotive variation, but also by conductivity variation.\* Acting on this principle, I have been able to construct an artificial retina. The sensitive receiver is contained inside a hollow spherical case, provided with a circular opening in front, in which a glass lens is placed, corresponding to the crystalline lens. You now see before you a complete model of an artificial eye.† When this is interposed in an electric circuit, with a sensitive galvanometer as indicator, you observe the response to a flash of light by the galvanometer deflection. I throw red, yellow, green and violet lights upon it in succession, and you see how it responds to all. Note how strong is the action of yellow light, the response to violet being relatively feeble. Indeed; the most striking peculiarity of this eye is that it can see lights not only some way beyond the violet, but also in regions far below the infra-red, in the invisible regions of electric radiation. It is in fact a *Tejometer* (Sanskrit *tej* = radiation), or universal radiometer.

Observe how each flash of invisible light I am producing with this electric radiation apparatus, calls forth an immediate response, and how the eye automatically recovers without external aid. This will show the possibility of an automatic receiver which will record Hertzian wave-messages without the intervention of the crude tapping device.

This retina has, as will be seen with regard to spectral vision, an enormous range, extending far beyond the visual limits. We can, however, reduce its powers to a merely human level by furnishing it

\* See 'On the Similarity of Effect of Electrical Stimulus on Inorganic and Living Substances.'—*Electrician*, Sept. 1900.

† I hope to publish a complete account of this instrument at a future date. The descriptions which follow are more detailed than time permitted on the 10th of May.

with a water lens, which, in its liquid constitution, approximates closer to the lens of the eye than does the glass substitute. In this case the, to us invisible, radiations are absorbed by the liquid, and do not reach the sensitive retina. Perhaps we do not sufficiently appreciate, especially in these days of space-signalling by Hertzian waves, the importance of that protective contrivance which veils our sense against insufferable radiance.



FIG. 14.—(a) Response curves of artificial retina for short periods of illumination followed by darkness. The ascending portions show the growing effect of light, the horizontal portion the balancing tetanic effect. The descending portion of the curve exhibits recovery during the absence of light. (b) Same in frog's retina (Waller).

I give here two sets of curves, one exhibiting the response of the artificial retina and the other of that of a frog, to show the general resemblance of the two (Fig. 14).

*Binocular  
Alternation  
of Vision.\**

I have referred to the fact that sometimes on the cessation of light, an after-oscillation is observed, which may correspond to the after-oscillations of the retina, and give a probable explanation of the phenomena of recurrent vision. When we have looked at a bright object for some time with one eye, we find, on closing both eyes, that the image of this object alternately appears and disappears. It was while studying this subject that I came upon the curious fact that the two eyes do not see equally well at a given instant, but take up, as it were, the work of seeing, and then (relatively speaking) resting, alternately. There is thus a relative retardation of half a period as regards maximum sensation in the two retinas. This may be seen, by means of a stereoscope, carrying, instead of stereophotographs, incised plates through which we look at light. The design consists of two slanting cuts at a suitable distance from each other. One cut, R, slants to the right, and the other, L, to the left (see Fig. 15). When the design is looked at through the stereoscope, the right eye will see, say R, and the left L; the two images

will appear superimposed, and we see an inclined cross. When the stereoscope is turned towards the sky, and the cross looked at steadily for some time, it will be found, owing to the alternation already referred to, that while one arm of the cross begins to be dim, the other becomes bright, and *vice versa*. The alternate fluctuations become far more conspicuous when the eyes are closed; the pure oscillatory after-effects of the strained sensitive molecules are then obtained in a most vivid manner. After looking through the stereoscope for ten seconds or more, the eyes are closed. The first effect observed is one of darkness, due to the rebound. Then one luminous arm of the cross first projects aslant the dark field, and then slowly disappears; after which the second (perceived by the other eye) shoots out suddenly in a direction athwart the first. This alternation proceeds for a long time, and produces the curious effect of two luminous blades crossing and re-crossing each other. Another method of bringing out the same facts in a still more striking manner, is to look at two different sets of writing, with the two eyes. The resultant effect is a blurr, due to superposition, and the inscription cannot be read with the eyes open. But on closing them, the composite image is analysed into its component parts, and thus we are enabled to read better with eyes shut than open!

You will thus see how, from observing the peculiarities of an artificial organ, we are led to discover unsuspected peculiarities in our own. We stand here on the threshold of a very extended inquiry, of which I can only say that as it has been possible to construct an artificial retina, so I believe it may not be impossible to imitate also other organs of sense.

*Effects of  
Chemical  
Reagents.*

We now return to the consideration of mechanical stimulus and the modification of its responses, as shown in our cell. We have seen the remarkable parallelism between organic and inorganic response under various conditions. There still remains the study of the effects of chemical reagents. For drugs profoundly modify the response of living substances. With respect to this function, they fall into three classes, some acting as stimulants, others as depressors, and yet others again as poisons, by which response is altogether killed. Amongst the last may be mentioned mercuric chloride, strong solutions of acids, and alkalies like potash. Again, drugs which in large doses become poisons, may, when applied in small quantities, act as stimulants.

It may be thought that to these phenomena, inorganic matter

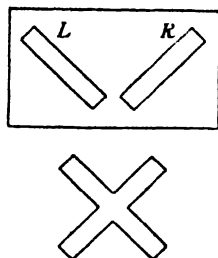


FIG. 15.—Stereoscopic design to show binocular alternation of vision.

could offer no parallel. For they involve possibilities which we have regarded as exclusively physiological. Accustomed in animal bodies to see the responsive pass into the irresponsible state at the moment of death, we look on this sequence as peculiar to the world of the living. And on this fact is based the supreme test by which physical and physiological phenomena are differentiated. That only can be called living which is capable of dying, we say, and death can be accelerated by the administration of poison. The sign of life as given by the electric pulses then wanes, till it ceases altogether. Molecular immobility—the rigor of death—supervenes, and that which was living is no longer alive.

Is it credible that we might, in like manner, kill inorganic response by the administration of poison? Could we by this means induce a condition of immobility in metals, so that, under its influence, their electric pulsations should wane and die out altogether?

Before we attempt the action of poisons let us study the exciting effect of stimulants. You observe in the galvanometer scale the



FIG. 16.—Curves showing stimulating action of  $\text{Na}_2\text{CO}_3$ . The three curves to the left show normal response; the four to the right increased response after addition of  $\text{Na}_2\text{CO}_3$ .

normal extent of response under successive uniform stimuli applied to one wire of the cell. I now add a few drops of sodium carbonate to the water in the cell and you observe the growing exaltation of the response. There are other stimulants besides this which would induce a still higher increase of sensibility, even to an astonishing degree\* (Fig. 16).

I now pass on to the effect of poisons. Any of the substances already enumerated may be used

as the toxic agent. I take a fresh cell, and first demonstrate before you its normal electrical pulsation. By means of a pipette I now inject into the cell the toxic dose. Its effect is at once evident to you. After a few preliminary flutterings the electric pulses cease to beat, and all our efforts, by intense stimulation to reawaken them, fail (Fig. 17).

But we may, sometimes at least, by the timely application of a suitable antidote, revive the dying response, as I do now, by an appropriate injection. See how the lethargy of immobility passes away; the pulse-throb grows stronger and stronger, and the response in our piece of metal becomes normal once more (Fig. 19).

There remains the very curious phenomenon, known not only to

\* The external resistance, as has been said previously, is kept very large, and the slight variation of the internal resistance of the cell has no effect on the deflection. The increased response can also be shown by capillary electrometer. Note also the disappearance of response by the influence of large dose.

students of physiological response but also in medical practice, that of the opposite effects produced by the same drug when given in large or in small doses. Here too we have the same phenomena reproduced

Before

After



FIG. 17.—Photographic record, showing the killing action of strong dose of KHO (1 per cent.) on tin. The electric response is abolished after the application of potash. Compare the effect of KHO on nerve in Fig. 18.

Before

After

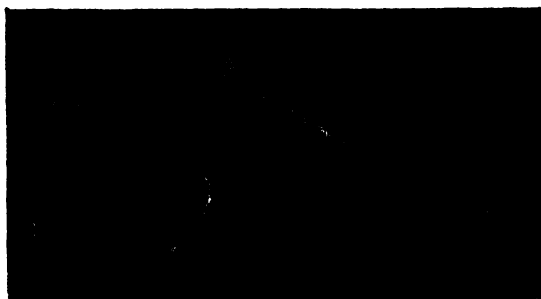


FIG. 18.—Killing action of KHO on electric response of nerve (Waller).

in an extraordinary manner in inorganic response (Fig. 20). The same reagent which becomes a poison in large quantities may act as a stimulant when applied in small doses.



I have shown you this evening autographic records of the history of stress and strain in the living and non-living. How similar are the writings! So similar indeed that you cannot tell one from the other apart. We have watched the responsive pulses wax and wane



FIG. 19.—(a) Normal response; (b) effect of poison; (c) revival by antidote.

in the one as in the other. We have seen response sinking under fatigue, becoming exalted under stimulants, and being killed by poisons, in the non-living as in the living.

Amongst such phenomena, how can we draw a line of demarcation, and say, "here the physical process ends, and there the physiological begins"? No such barriers exist.

Before

After

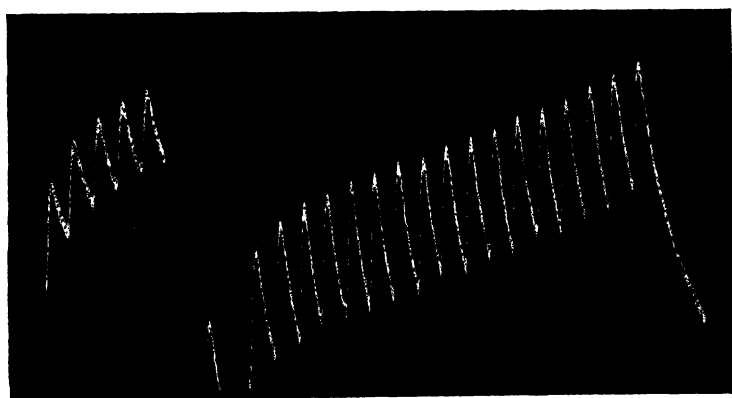


FIG. 20.—Photographic record, showing stimulating effect of small dose of KHO (0.2 per cent.). Compare with Fig. 17.

Do not the two sets of records tell us of some property of matter common and persistent? Do they not show us that the responsive processes, seen in life, have been foreshadowed in non-life?—that the physiological is, after all, but an expression of the physical?—

that there is no abrupt break, but one uniform and continuous march of law?

If it be so, we shall but turn with renewed courage to the investigation of mysteries which have long eluded us. For every step of science has been made by the inclusion of what seemed contradictory or capricious in a new and harmonious simplicity. Her advances have been always towards a clearer perception of underlying unity in apparent diversity.

It was when I came upon the mute witness of these self-made records, and perceived in them one phase of a pervading unity that bears within it all things—the mote that quivers in ripples of light, the teeming life upon our earth, and the radiant suns that shine above us—it was then that I understood for the first time a little of that message proclaimed by my ancestors on the banks of the Ganges thirty centuries ago—

“They who see but one, in all the changing manifoldness of this universe, unto them belongs Eternal Truth—unto none else, unto none else!”

Friday, May 24, 1901.

THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

RICHARD T. GLAZEBROOK, Esq., M.A. D.Sc. F.R.S. M.R.I.

*The Aims of the National Physical Laboratory.*

THE idea of a physical laboratory in which problems bearing at once on science and on industry might be solved is comparatively new. The Physikalisch-Technische Reichsanstalt, founded in Berlin by the joint labours of Werner von Siemens and von Helmholtz during the years 1883-87, was perhaps the first. It is less than ten years since Dr. Lodge, in his address to Section A of the British Association, outlined the scheme of work for such an institution here in England. Nothing came of this; a committee met and discussed plans, but it was felt to be hopeless to approach the Government, and without Government aid there were no funds.

Four years later, however, the late Sir Douglas Galton took the matter up. In his address to the British Association in 1895, and again in a paper read before Section A, he called attention to the work done for Germany by the Reichsanstalt and to the crying need for a similar institution in England.

The result of this presidential pronouncement was the formation of a committee which reported at Liverpool, giving a rough outline of a possible scheme of organisation. A petition to Lord Salisbury followed, and as a consequence a Treasury Committee, with Lord Rayleigh in the chair, was appointed to consider the desirability of establishing a National Physical Laboratory. The committee examined more than thirty witnesses, and then reported unanimously "that a public institution should be founded for standardising and verifying instruments for testing materials and for the determination of physical constants."

It is natural to turn to the words of those who were instrumental in securing the appointment of this committee, and to the evidence it received, in any endeavour to discuss its aim. As was fitting, Sir Douglas Galton was the first witness to be called. It is a source of sorrow to his many friends that he has not lived to see the Laboratory completed.

And here I may refer to another serious loss which, in the last few days, the Laboratory has sustained. Sir Courtenay Boyle was a

member of Lord Rayleigh's committee, and as such was convinced of the need for the Laboratory and of the importance of the work it could do. He took an active part in its organisation, sparing neither time nor trouble; he intended that it should be a great institution, and he had the will and the power to help. The country is the poorer by his sudden death.

Let me now quote some of Sir Douglas Galton's evidence. "Formerly our progress in machinery," he says, "was due to accuracy of measurement, and that was a class of work which could be done, as Whitworth showed, by an educated eye and educated touch. But as we advance in the applications of science to industry we require accuracy to be carried into matters which cannot be so measured. . . . In the more delicate researches which the physical, chemical and electrical student undertakes, he requires a ready means of access to standards to enable him to compare his own work with that of others." Or again, "My view is that if Great Britain is to retain its industrial supremacy we must have accurate standards available to our research students and to our manufacturers. I am certain that if you had them our manufacturers would gradually become very much more qualified for advancing our manufacturing industry than they are now. But it is also certain that you cannot separate some research from a standardising department." Then, after a description of the Reichsanstalt, he continues, "What I would advocate would be an extension of Kew in the direction of the second division of the Reichsanstalt, with such auxiliary research in the establishment itself as may be found necessary." The second division is the one which takes charge of technical and industrial questions. Professor Lodge, again, gave a very valuable summary of work which ought to be done.

It is now realised, at any rate by the more enlightened of our leaders of industry, that science can help them. This fact, however, has been grasped by too few in England; our rivals in Germany and America know it well, and the first aim of the Laboratory is to bring its truth home to all, to assist in promoting a union which is certainly necessary if England is to retain her supremacy in trade and in manufacture, to make the forces of science available for the nation, to break down by every possible means the barrier between theory and practice, and to point out plainly the plan which must be followed unless we are prepared to see our rivals take our place.

"Germany," an American writer who has recently made a study of the subject has said, "is rapidly moving towards industrial supremacy in Europe. One of the most potent factors in this notable advance is the perfected alliance between science and commerce existing in Germany. Science has come to be regarded there as a commercial factor. If England is losing her supremacy in manufactures and in commerce, as many claim, it is because of English conservatism and the failure to utilise to the fullest extent the lessons taught by science, while Germany, once the country of

dreamers and theorists, has now become intensely practical. Science there no longer seeks court and cloister, but is in open alliance with commerce and industry." It is our aim to promote this alliance in England, and for this purpose the National Physical Laboratory has been founded.

It is hardly necessary to quote chapter and verse for the assertion that the close connection between science and industry has had a predominant effect on German trade. If authority is wanted, I would refer to the history of the anilin dye manufacture, or, to take a more recent case, to the artificial indigo industry, in which the success of the Badische Company has recently been so marked. The factory at Ludwigshaven started thirty-five years ago with thirty men; it now employs more than 6000 and has on its staff 148 trained scientific chemists. And now, when it is perhaps too late, the Indian planters are calling in scientific aid, and the Indian Government are giving some 3500*l.* a year in investigation.

As Professor Armstrong, in a recent letter to the *Times*, says, "The truly serious side of the matter, however, is not the prospective loss of the entire indigo industry so much as the fact that an achievement such as that of the Badische Company seems past praying for here." Another instance is to be found in the German exhibit of scientific instruments at the Paris Exhibition, of which a full account appeared in the pages of *Nature*.

And now, having stated in general terms the aims of the Laboratory and given some account of the progress in Germany, let me pass to some description of the means which have been placed at our disposal to realise those aims. I then wish, if time permits, to discuss in fuller detail some of the work which it is hoped we may take up immediately.

The Laboratory is to be at Bushy House, Teddington. I will pass over the events which led to the change of site from the Old Deer Park at Richmond to Bushy. It is sufficient to say that at present Kew Observatory in the Deer Park will remain as the Observatory department of the Laboratory, and that most of the important verification and standardisation work which in the past has been done there will still find its home in the old building.

Bushy House was originally the official residence of the Ranger of Bushy Park. Queen Anne granted it in 1710 to the first Lord Halifax. In 1771 it passed to Lord North, being then probably rebuilt. Upon the death of Lord North's widow in 1797, the Duke of Clarence, afterwards William IV., became Ranger; after his death in 1837 it was granted to his widow, Queen Adelaide, who lived there until 1849. At her death it passed to the Duc de Nemours, son of King Louis Philippe, and he resided there at intervals until 1896.

In spite of this somewhat aristocratic history, it will make an admirable Laboratory. A description of the Laboratory, with illustrations, will be found in *Nature*, vol. lxxiii. p. 300.

The floor space available is much less than that of the Reichsanstalt. But size alone is not an unmixed advantage; there is much to be said in favour of gradual growth and development, provided the conditions are such as to favour growth. Personally I should prefer to begin in a small way if only I felt sure I was in a position to do the work thoroughly: but there is danger of starvation. Even with all the help we get in freedom from rent and taxes, outside repairs and maintenance, the sum at the disposal of the committee is too small.

Science is not yet regarded as a commercial factor in England. Is there no one who realises the importance of the alliance, who will come forward with more ample funds to start us on our course with a fair prospect of success? One candid friend has recently told us in print that the new institution is on such a microscopic scale that its utility in the present struggle is more than doubtful. Is there no statesman who can grasp the position and see that with, say, double the income the chances of our doing a great work would be increased a hundredfold?

The problems we have to solve are hard enough: give us means to employ the best men and we will answer them; starve us and then quote our failure as showing the uselessness of science applied to industry!

There is some justice in the criticism of one of our technical papers. I have recently been advertising for assistants, and a paper in whose columns the advertisement appears writes, "The scale of pay is certainly not extravagant. It is, however, possible that the duties will be correspondingly light."

Now let me illustrate these aims by a more detailed account of some of the problems of industry which have been solved by the application of science, and then of some others which remain unsolved and which the Laboratory hopes to attack. The story of the Jena Glass Works is most interesting; I will take it first.

An exhibition of scientific apparatus took place in London in 1876. Among the visitors to this was Professor Abbe, of Jena, and in a report he wrote on the optical apparatus he called attention to the need for progress in the art of glass making if the microscope were to advance, and to the necessity for obtaining glasses having a different relation between dispersion and refractive index than that found in the material at the disposal of opticians. Stokes and Harcourt had already made attempts in this direction, but with no marked success.

In 1881 Abbe and Schott, at Jena, started their work. Their undertaking, they write five years later in the first catalogue of their factory, arose out of a scientific investigation into the connection between the optical properties of solid amorphous fluxes and their chemical constitution. When they began their work, some six elements only entered into the composition of glass. By 1888 it had been found possible to combine with these, in quantities up to

about 10 per cent., twenty-eight different elements, and the effect of each of these on the refractive index and dispersion had been measured. Thus, for example, the investigators found that by the addition of boron the ratio of the length of the blue end of the spectrum to that of the red was increased; the addition of fluorine, potassium or sodium produced the opposite result.

Now in an ordinary achromatic lens of crown and flint, if the total dispersion for the two be the same, then for the flint glass the dispersion of the blue end is greater, that of the red less than for the crown; thus the image is not white: a secondary spectrum is the result.

Abbe showed, as Stokes and Harcourt had shown earlier, that by combining a large proportion of boron with the flint, its dispersion was made more nearly the same as that of the crown, while by replacing the silicates in the crown glass by phosphates, a still better result was obtained, and by the use of three glasses three lines of the spectrum could be combined; the spectrum outstanding was a tertiary one, and much less marked than that due to the original crown and flint glass. The modern microscope became possible.

The conditions to be satisfied in a photographic lens differ from those required for a microscope. Von Seidel had shown that with the ordinary flint and crown glasses the conditions for achromatism and for flatness of field cannot be simultaneously satisfied. To do this we need a glass of high refractive index and low dispersive power, or *vice versa*; in ordinary glasses these two properties rise and fall together. By introducing barium into the crown glass a change is produced in this respect. For barium crown the refractive index is greater and the dispersive power less than for soft crown.

With two such glasses, then, the field can be achromatic and flat. The wonderful results obtained by Dallmeyer and Ross in this country, by Zeiss and Steinheil in Germany, are due to the use of these new glasses. They have also been applied with marked success to the manufacture of the object-glasses of large telescopes.

But the Jena glasses have other uses besides optical. "About twenty years ago"—the quotation is from the catalogue of the German exhibition—"the manufacture of thermometers had come to a dead stop in Germany, thermometers being then invested with a defect, their liability to periodic changes, which seriously endangered German manufacture. Comprehensive investigations were then carried out by the Normal Aichungs Commission, the Reichanstalt and the Jena Glass Works, and much labour brought the desired reward."

The defect referred to was the temporary depression of the ice point which takes place in all thermometers after heating. Let the ice point of a thermometer be observed; then raise the thermometer to, say, 100°, and again observe the ice point as soon as possible afterwards; it will be depressed below its previous position. In

some instruments of Thuringian glass a depression of as much as  $0^{\circ}\cdot65$  C. had been noted. For scientific purposes such an instrument is quite untrustworthy. If it be kept at, say,  $15^{\circ}$ , and then immersed in a bath at  $30^{\circ}$ , its reading will be appreciably different from that which would be given if it were first raised to, say,  $50^{\circ}$ , allowed to cool quickly just below  $30^{\circ}$ , and then put into the bath. This was the defect which the investigators set themselves to cure.

Table I. gives some details as to thermometers.

TABLE I.  
DEPRESSION OF FREEZING POINT FOR VARIOUS THERMOMETERS.

								Degrees.
Humboldt, 1835	..	..	..	..	..	..	..	0·06
Greiner, 1872	..	..	..	..	..	..	..	0·38
Schultzer, 1875	..	..	..	..	..	..	..	0·44
Rappa, 1878	..	..	..	..	..	..	..	0·65
English glass	..	..	..	..	..	..	..	0·15
Verre Dur	..	..	..	..	..	..	..	0·08
16'''	..	..	..	..	..	..	..	0·05
59'''	..	..	..	..	..	..	..	0·02

#### ANALYSIS OF GLASSES.

	SiO <sub>2</sub>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	ZnO	B <sub>2</sub> O <sub>3</sub>
16'''	67·5	14	7	2·5	7	2
59'''	72	11	—	5	—	12

Weber had found in 1883 that glasses which contain a mixture of soda and potash give a very large depression. He made a glass free from soda with a depression of  $0^{\circ}\cdot1$ . The work was then taken up by the Aichungs Commission, the Reichsanstalt and the Jena factory. Weber's results were confirmed. An old thermometer of Humboldt's, containing 0·86 per cent. of soda and 20 per cent. of potash, had a depression of  $0^{\circ}\cdot06$ , while a new instrument, in which the percentages were 12·7 per cent. and 10·6 per cent. respectively, had a depression of  $0^{\circ}\cdot65$ .

An English standard, with 1·5 per cent. of soda and 12·3 per cent. of potash, gave a depression of  $0^{\circ}\cdot15$ , while a French "verre dur" instrument, in which these proportions were reversed, gave only  $0^{\circ}\cdot08$ .

It remained to manufacture a glass which should have a low depression and at the same time other satisfactory properties. The now well-known glass 16''' is the result. Its composition is shown in the Table.

The fact that there was an appreciable difference between the scale of the 16''' glass and that of the air thermometer led to further investigations, and another glass 59''', a borosilicate containing 12 per cent. of boron, was the consequence. This glass has a still smaller depression.

Previous to 1888 Germany imported optical glass. At that date



nearly all the glass required was of home manufacture. Very shortly afterwards an export trade in raw glass began, which in 1898 was worth 30,000*l.* per annum, while the value of optical instruments, such as telescopes, field-glasses and the like, exported that year was 250,000*l.* Such are the results of the application of science, i. e. organised common sense, to a great industry. The National Physical Laboratory aims at doing the like for England.

I have thus noted very briefly some of the ways in which science has become identified with trade in Germany, and have indicated some of the investigations by which the staff of the Reichsanstalt and others have advanced manufactures and commerce.

Let us turn now to the other side, to some of the problems which remain unsolved, to the work which our Laboratory is to do and by doing which it will realise the aims of its founders.

The microscopic examination of metals was begun by Sorby in 1864. Since that date many distinguished experimenters, Andrews, Arnold, Ewing, Martens, Osmond, Roberts-Austen, Stead and others, have added much to our knowledge. I am indebted to Sir W. Roberts-Austen for the slides which I am about to show you to illustrate some of the points arrived at. Professor Ewing a year ago laid before the Royal Institution the results of the experiments of Mr. Rosenhain and himself.

This microscopic work has revealed to us the fact that steel must be regarded as a crystallised igneous rock. Moreover, it is capable, at temperatures far below its melting point, of altering its structure completely, and its mechanical and magnetic properties are intimately related to its structure. The chemical constitution of the steel may be unaltered, the amounts of carbon, silicon, manganese, &c., in the different forms remain the same, but the structure changes, and with it the properties of the steel.

Sections of the same steel polished and etched after various treatments show striking differences. For instance, if a highly carburised form containing 1.5 per cent. of carbon be cooled down from the liquid state, the temperature being read by the deflection of a galvanometer needle in circuit with a thermopile, the galvanometer shows a slowly falling temperature till we reach 1380° C., when solidification takes place; the changes which now go on take place in solid metal. After a time the temperature again falls until we reach 680°, when there is an evolution of heat; had the steel been free from carbon there would have been evolution of heat at 895° and again at 766°. Now throughout the cooling, molecular changes are going on in the steel. By quenching the steel suddenly at any given temperature we can check the change and examine microscopically the structure of the steel at the temperature at which it was checked.

[Slides were shown representing the microscopic structures of steels subjected to different treatment as regards temperature and annealing.]

These slides are sufficient to call attention to the changes which occur in solid iron, changes whose importance is now beginning to be realised. On viewing them it is a natural question to ask how all the other properties of iron related to its structure; can we by special treatment produce a steel more suited to the shipbuilder, the railway engineer or the dynamo maker than any he now possesses?

These marked effects are connected with variations in the condition of the carbon in the iron; can equally or possibly more marked changes be produced by the introduction of some other element? Guillaume's nickel steel, with its small coefficient of expansion, appears to have a future for many purposes; can it or some modification be made still more useful to the engineer?

We owe much to the investigations of the Alloys Research Committee of the Institution of Mechanical Engineers. Their distinguished chairman holds the view that the work of that committee has only begun, and that there is scope for such research for a long time to come at the National Physical Laboratory. The executive committee have accepted this view by naming as one of the first subjects to be investigated the connection between the magnetic quality and the physical, chemical and electrical properties of iron and its alloys, with a view especially to the determination of the conditions for low hysteresis and non-agency properties.

At any rate we may trust that the condition of affairs mentioned by Mr. Hadfield in his evidence before Lord Rayleigh's Commission which led a user of English steel to specify that before the steel could be accepted it must be stamped at the Reichsanstalt, will no longer exist.

The subject of wind pressure, again, is one which has occupied this committee's attention to some extent. The Board of Trade rules require that in bridges and similar structures (1) a maximum pressure of 56 lbs. per square foot be provided for; (2) that the effective surface on which the wind acts should be assumed as from once to twice the area of the front surface, according to the extent of the openings in the lattice girders; (3) that a factor of safety of 4 for the iron work and of 2 for the whole bridge overturning be assumed. These recommendations were not based on any special experiments. The question had been investigated in part by the late Sir W. Siemens.

During the construction of the Forth Bridge Sir B. Baker conducted a series of observations. The results of the first two years' observations are shown in Table II., taken from a paper read at the British Association in 1884. Three gauges were used.

In No. 1 the surface on which the wind acted was about  $1\frac{1}{2}$  square feet in area; it was swivelled so as always to be at right angles to the wind. In No. 2 the area of surface acted on was of the same size, but it was fixed with its plane north and south. No. 3 was also fixed in the same direction, but it had 200 times the area, its surface being 300 square feet.

TABLE II.

Revolving Gauge.		Small Fixed Gauge.		Large Fixed Gauge.	
Mean Pressure.		Easterly.	Westerly.	Easterly.	Westerly.
lb.	lb.	lb.	lb.	lb.	lb.
0 to 5	3.09	3.47	2.92	2.04	1.9
5 to 10	7.58	4.8	7.7	3.54	4.75
10 to 15	12.4	6.27	13.2	4.55	8.26
15 to 20	17.06	7.4	17.9	5.5	12.66
20 to 25	21.0	12.25	22.75	8.6	19.0
25 to 30	27.0		28.5		18.25
30 to 35	32.5		38.5		21.5
Above 65			41.0		35.25
(One observation only above 32.5).					

In preparing the table the mean of all the readings of the revolving gauge between 0 and 5, 5 and 10, &c., lbs. per square foot have been taken, and the mean of the corresponding readings of the small fixed gauge, and the large fixed gauge set opposite, these being arranged for easterly and westerly winds.

Two points are to be noticed : (1) only one reading of more than 32.5 lbs. was registered, and this, it is practically certain, was due to faulty action in the gauge.

Sir B. Baker has kindly shown me some further records with a small gauge.

According to these, pressures of more than 50 lbs. have been registered on three occasions since 1886. On two other occasions the pressures, as registered, reached from 40 to 50 lbs. per square foot. But the table, it will be seen, enables us to compare the pressure on a small area with the average pressure on a large area, and it is clear that in all cases the pressure per square foot as given by the large area is much less than that deduced from the simultaneous observations on the small area.

The large gauge became unsafe in 1896 and was removed ; but the observations for the previous ten years entirely confirm this result, the importance of which is obvious. The same result may be deduced from the Tower Bridge observations. Power is required to raise the great bascules, and the power needed depends on the direction of the wind. From observations on the power some estimate of the average wind pressure on the surface may be obtained, and this is found to be less than the pressure registered by the small wind gauges. Nor is the result surprising, when the question is looked at as a hydrodynamical problem ; the lines of fluid near a small obstacle will differ from those near a large one, and the distribution of pressure over the large area will not be uniform. Sir W. Siemens is said to have found places of negative pressure near such an obstacle.

As Sir J. Wolfe Barry has pointed out, if the average of 56 lbs. to the square foot is excessive, then the cost and difficulty of erection of large engineering works is being unnecessarily increased. Here is a problem well worthy of attention, and about which but little is known. The same, too, may be said about the second of the Board of Trade rules. What is the effective surface over which the pressure is exerted on a bridge? On this again our information is but scanty. Sir B. Baker's experiments for the Forth Bridge led him to adopt as his rule, Double the plane surface exposed to the wind and deduct 50 per cent. in the cases of tubes. On this point again further experiments are needed.

To turn from engineering to physics. In metrology, as in many other branches of science, difficulties connected with the measurement of temperature are of the first importance.

I was asked some little time since to state, to a very high order of exactness, the relation between the yard and the metre. I could not give the number of figures required. The metre is defined at the freezing point of water, the yard at a temperature of 62° F. When a yard and a metre scale are compared they are usually at about the same temperature; the difficulty of comparison is enormously increased if there be a temperature difference of 30° F. between the two scales. Hence we require to know the temperature coefficients of the two standards. But that of the standard yard is not known; it is doubtful, I believe, if the composition of the alloy of which it is made is known, and in consequence Mr. Chaney has mentioned the determination of coefficients of expansion as one of the investigations which it is desirable that the Laboratory should undertake.

Or, again, take thermometry. The standard scale of temperature is that of the hydrogen thermometer; the scale in practical use in England is the mercury in flint glass scale of the Kew standard thermometers. It is obvious that it is of importance to science that the difference between the scales should be known, and various attempts have been made to compare them. But the results of no two series of observations which have been made agree satisfactorily. The variations arise probably in great measure from the fact that the English glass thermometer, as ordinarily made and used, is incapable of the accuracy now demanded for scientific investigations. The temporary depression of the freezing point already alluded to in discussing the Jena glass is too large; it may amount to three- to four-tenths of a degree when the thermometer is raised 100°. Thus the results of any given comparison depend too much on the immediate past history of the thermometer employed, and it is almost hopeless to construct a table, accurate, say, to .01, which will give the difference between the Kew standard and the hydrogen scale, and so enable the results of former work in which English thermometers were used to be expressed in standard degrees.

This is illustrated by Table III., which gives the differences as found (1) by Rowland; (2) Guillaume; (3) Wiebe, between a Kew thermometer and the air thermometer.

TABLE III.—VALUES OF CORRECTIONS TO THE ENGLISH GLASS THERMOMETER SCALE TO GIVE TEMPERATURES ON THE GAS THERMOMETER SCALE FOUND BY VARIOUS OBSERVERS.

Temp.	Rowland.	Ga'illaume.	Wiebe.
°	°	°	°
0	0	0	0
10	— ·03	— ·009	+ ·03
20	— ·05	— ·009	+ ·00
30	— ·06	— ·002	+ ·02
40	— ·07	+ ·007	+ ·09
50	— ·07	+ ·016	+ ·14
60	— ·06	+ ·014	
70	— ·04	+ ·028	
80	— ·02	+ ·026	
90	— ·01	+ ·017	
100	0	0	

It is clearly important to establish in England a mercury-scale of temperatures which shall be comparable with the hydrogen scale, and it is desirable to determine as nearly as may be the relation between this and the existing Kew scale.

I am glad to say that in the first endeavour we have secured the valuable co-operation of Mr. Powell, of the Whitefriars Works, and that the first specimens of glass he has submitted to us bid fair to compare well with 16".

Another branch of thermometry in which there is much to do is the measurement of high temperature. Professor Callendar has explained here the principles of the resistance thermometer, due first to Sir W. Siemens. Sir W. C. Roberts-Austen has shown how the thermopile of Le Chatellier may be used for the measurement of high temperatures. There is a great work left for the man who can introduce these or similar instruments to the manufactory and the forge, or who can improve them in such a manner as to render their uses more simple and more sure. Besides, at temperatures much over 1000° C., the glaze on the porcelain tube of the pyrometer gives way.

So far we have discussed new work, but there is much to be done in extending a class of work which has gone on quietly and without much show for many years at the Kew Observatory. Thermometers and barometers, wind gauges and other meteorological apparatus, watches and chronometers, and many other instruments are tested there in great numbers, and the value of the work is undoubted. The competition among the best makers for the first place, the best watch of the year, is most striking and affords ample testimony to the importance of the work.

Work of this class we propose to extend. Thus, there is no place where pressure gauges or steam indicators can be tested. It is

intended to take up this work, and for this purpose a mercury pressure column is being erected.

Again, there are the ordinary gauges in use in nearly every engineering shop. These, in the first instance, have probably come from Whitworth's, or nowadays, I fear, from Messrs. Pratt and Whitney or Browne and Sharpe, of America. They were probably very accurate when new, but they wear, and it is only in comparatively few large shops that means exist for measuring the error and for determining whether the gauge ought to be rejected or not. Hence arise difficulties of all kinds. Standardisation of work is impossible.

In another direction a wide field is offered in the calibration and standardisation of glass measuring vessels of all kinds, flasks, burettes, pipettes, &c., used by chemists and others. At the request of the Board of Agriculture we have already arranged for the standardisation of glass vessels used in the Babcock method of measuring the butter fat in milk, and in a few months many of these have passed through our hands. We are now being asked to arrange for testing the apparatus for the Gerber and Leffman-Beam methods, and this we have promised to do when we are settled at Bushy. Telescopes, opera-glasses, sextants, and other optical appliances, are already tested at Kew, but this work can, and will, be extended. Photographic lenses are now examined by eye; a photographic test will be added, and I trust the whole may be made more useful to photographers.

I look to the co-operation of the Optical Society to advise how we may be of service to them in testing spectacles, microscope lenses and the like. The magnetic testing of specimens of iron and steel, again, offers a fertile field for inquiry. If more subjects are needed it is sufficient to turn over the pages of the evidence given before Lord Rayleigh's Commission, or to look to the reports which have been prepared by various bodies of experts for the executive committee.

In electrical matters there are questions relating to the fundamental units on which, in Mr. Trotter's opinion, we may help the officials of the Board of Trade. Standards of capacity are wanted; those belonging to the British Association will be deposited at the Laboratory. Standards of electromagnetic induction are desirable; questions continually arise with regard to new forms of cells other than the standard Clark cell, and in a host of other ways work will be found.

I have gone almost too much into detail. It has been my wish to state in general terms the aims of the Laboratory to make the advance of physical science more readily available for the needs of the nation, and then to illustrate the way in which it is intended to attain those aims. I trust I may have shown that the National Physical Laboratory is an institution which may deservedly claim the cordial support of all who are interested in real progress.

[R. T. G.]

## HODGKINS TRUST.

ESSAY BY MISS AGNES M. CLERKE.

### *Low-Temperature Research at the Royal Institution, 1893-1900.*

EARLY in 1895 the late Mr. Thomas G. Hodgkins presented to the Royal Institution a sum of 100,000 dollars,\* as a source of income to be employed in the "investigation of the relations and co-relations existing between man and his Creator." On the ensuing 6th of February the Managers resolved to carry out the intentions of the donor, by devoting the resources thus placed at their disposal to the work of the Institution, which, having for its aim the attainment of truth, constitutes an effective means of "directing thought to the source of all knowledge."

"In der Schöpfung," Kepler wrote, "greife ich Gott, gleichsam mit Händen"; and Faraday reflected, "with wondering awe," on the powers of interrogating nature "given by the Almighty to man." These great men were no mere transcendentalists. The lofty aspect under which they viewed physical research may indeed be temporarily forgotten, but cannot permanently be lost sight of, for it corresponds to an invincible human instinct. Law formulates intelligent purpose; and the laws of nature are an expression of the Will of God. In tracing them out, man seeks, more or less consciously, the infinite; and his capability of tracing them is derived solely from the analogy of his mind with the Creative Mind, which designed a universe assumed by the necessities of thought to be a "cosmos"—an orderly arrangement, such as his faculties can apprehend. Were it unplanned, or planned according to a method incomprehensible by human reason, science would have no *locus standi*: life should be conducted on purely empirical principles. As a fact, however, we find the world essentially intelligible; and, by striving to enlarge the limits of its intelligibility, we promote the purpose of the Creator in placing us there, and, following in the track of His primal conceptions, bring our inchoate ideas more and more into harmony with them. The object of the present paper is to show what has been done towards this end at the Royal Institution, during the last seven years, under the terms of the Hodgkins Trust.

Research at low temperatures has long been recognised as the characteristic task of the establishment. Resuming, after the lapse of a third of a century, the traditions of Davy and Faraday, Professor Dewar gave a new stamp to his operations by the enlargement of

\* Investment in Consols amounts to 17,986*l.* 1*s.*

their scale. They have been conducted, not for the mere purpose of scoring experimental successes by liquefying intractable gases, but with a view to extensive and profound investigations of the properties of matter under conditions previously unattainable. The realisation of these conditions, however, demands a profuse outlay of labour, time, and money, to say nothing of the risks incurred through the rebellion of natural forces against rigid mechanical constraint. Hence, a colossal equipment, disposed of by an individual of untiring energy, united to courage and inventiveness of no common order, was indispensable for the furtherance of this important enterprise; and nowhere has the combination been rendered so thoroughly effective as in the laboratory of the Royal Institution. Its effectiveness, however, has not been due to the generosity of one benefactor alone. Many have contributed to it. The munificence of the Goldsmiths' Company has twice brought timely relief in financial straits; the donations of private individuals have furnished indispensable supplies, and merit emphatic and grateful acknowledgment. The coincidence is noteworthy that the only considerable sum received by the Royal Institution for the endowment of research has come from a fellow-countryman of its versatile and far-seeing founder. What Count Rumford had begun Mr. Hodgkins designedly continued, and by sharing his subsidies between the Royal Institution of Great Britain and the Smithsonian Institution of Washington, he evidently proposed to invite the cordial co-operation of the two great English-speaking peoples for the investigation of those subjects in which he was so deeply interested.

The stage of the campaign arrived at when the Hodgkins fund became available for its prosecution may be described in a few words. All the known gases, except hydrogen and fluorine, had been reduced to liquids in a statical condition, and of these, liquid oxygen alone had refused to solidify when evaporated under diminished pressure. A point of cold had been reached only  $73^{\circ}$  C. above the absolute zero ( $-273^{\circ}$ ), and the altered electrical and chemical relations of various substances cooled to  $-182^{\circ}$  had been investigated. The observed progressive decrease, with increase of cold, in the electrical resistance of pure metals, seemed to betoken its total disappearance near the absolute zero, while alloys lost little of their resistivity, and carbon followed an inverse course of change. The curious individualities, in this respect, of different metals were also noted. Thus, the resistivity of iron is reduced to one twenty-third, that of copper only to one-eleventh, by lowering its temperature from  $+100^{\circ}$  to  $-197^{\circ}$ , at which point an iron wire actually conducts better than one of the finest copper when ordinarily warm. In these inquiries Professor J. A. Fleming co-operated with Professor Dewar. On December 10, 1891, the magnetic quality of liquid oxygen was discovered by Professor Dewar. Other well-known properties of the gas proved to be equally persistent after condensation. Liquid, like gaseous oxygen, is a bad conductor of heat and electricity, while



transparent to thermal radiations. Its absorption-spectrum, too, is virtually the same as that of the gas; so that it could be inferred that the molecular constitution of the element was little affected by change of state.

The practical difficulties impeding the preservation and observation of frigid liquids were, in great measure, overcome by Professor Dewar's invention of vacuum-coated vessels for storing them. By their means the access of heat, whether by convection or by radiation, was so effectually checked that evaporation shrank at once to one-fifth its former amount, and the deposition of a thin film of mercury on the surface of the containing glass still further lessened the waste. Added refinements of construction brought it down to a mere fraction of what it had been in unprotected receptacles, and the durability of volatile fluids thus obtained a thirty-fold extension. Tranquillity was besides given to them, ebullition ceased, and they could be manipulated with ease. This essential improvement was effected late in 1892. Thus, at the beginning of the septennial period we have now to consider, a steady and continuous advance was in progress, and much new territory had been annexed and explored. A tract, it is true, lay beyond, not wide, but most arduous to penetrate; yet there was a hope of its thorough conquest through the amelioration of methods and the experience acquired in their application.

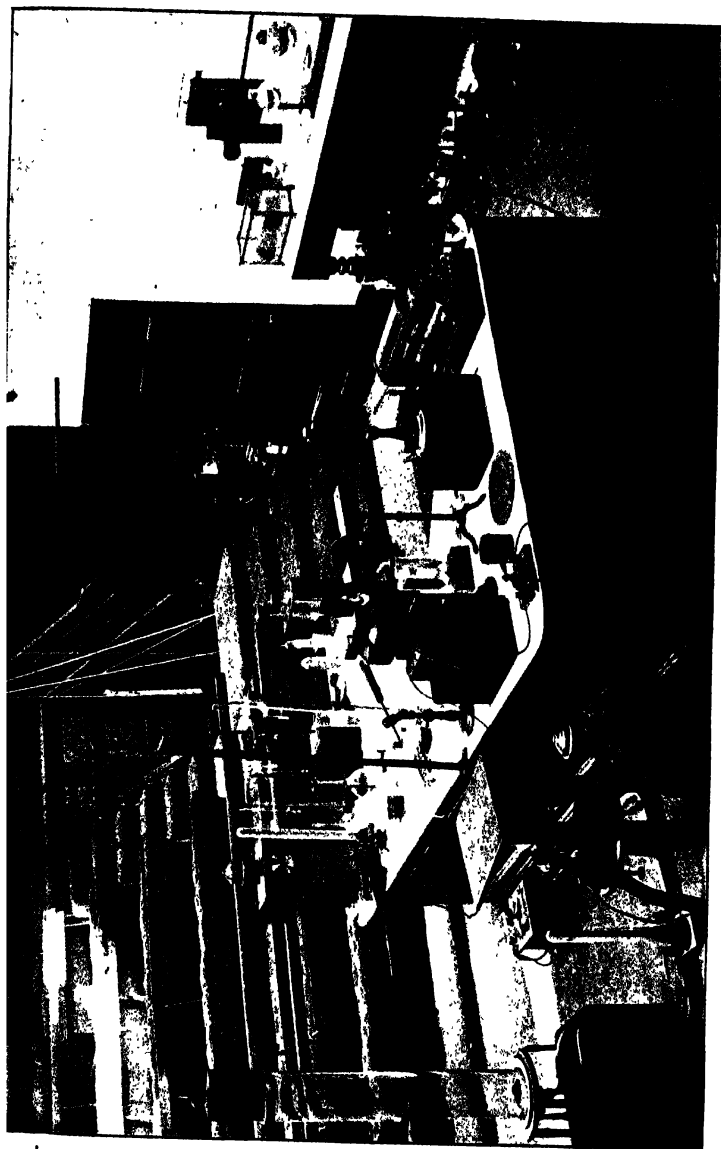
#### LIQUEFACTION OF HYDROGEN.

The main outstanding problem was the condensation of hydrogen. This is the lightest of known substances, yet it resembles a metal in being strongly electro-positive; in being a conductor of heat and electricity; and in forming, with palladium, sodium and potassium, compounds possessing some of the properties of alloys. Upon these grounds Faraday based the forecast that solid hydrogen would show metallic lustre. Its liquefaction was first demonstrated by M. Wroblewski, of Cracow, in January 1884. A froth of hydrogen became momentarily visible when the gas, cooled to the temperature of nitrogen boiling *in vacuo*, was suddenly released from a pressure of 180 atmospheres. This evasive appearance was reproduced by M. Olszewski; but neither experimenter succeeded in obtaining the liquid in tangible form. This was accomplished at the Royal Institution, as the outcome of a long series of efforts, frequently baffled, and persistently renewed. The conditions that had to be met were approximately known through Wroblewski's determination, by the aid of Van der Waal's formula, of the critical constants of hydrogen. He fixed the temperature *sine quâ non* (as it may be called) at  $-240^{\circ}\text{C.}$ , the corresponding pressure at 13 atmospheres, and the boiling point at  $-250^{\circ}$ . With these conditions, Professor Dewar made in 1894 a preliminary attempt to grapple, by mixing a small percentage of air or nitrogen with hydrogen, and thus producing an artificial gas capable of liquefaction by the use of liquid air. This

gaseous blend, subjected to powerful pressure at a temperature of  $-200^{\circ}\text{C}$ ., and then permitted to expand, gave rise to a degree of cold below any previously attained, and there resulted a deposit of solid air, together with a clear liquid of small density, too volatile for collection by any available device. This was, doubtless, the first sample of genuinely liquefied hydrogen ever exhibited to view.

Professor Dewar's object, however, was not merely to catch sight of liquid hydrogen, but to get hold of it. Enclosed in a glass tube, under pressure, it still remained comparatively inaccessible. Until it could be made to accumulate, at its boiling-point, in open vacuum-vessels, no satisfactory study of its nature was feasible. This goal was finally reached through the introduction of the regenerating coil. The principle of self-intensification had been, in 1857, applied by Siemens to the production of cold. In subsequent years its efficacy in this direction was turned to account for industrial purposes by Coleman, Solvay, Linde and others; while Dr. Kamerlingh Onnes had recourse to it in his cryogenic laboratory at Leiden in 1894. The prompt and copious liquefaction of refractory gases thus became an ordinary operation; but it was only at the Royal Institution that the facilities secured were made to serve for largely widening the scope of research.

In December 1895, Professor Dewar read a paper before the Chemical Society describing the mode of production and use of a liquid hydrogen jet. Owing to the rapid movement of the condensing gas, and the low specific gravity of the resultant liquid, attempts to collect it were fruitless; but, with better isolation and more perfectly adapted vacuum-tubes, their future success was anticipated. Meanwhile, research at some  $20^{\circ}$  or  $30^{\circ}$  above absolute zero was already practicable, by using a liquid-hydrogen spray as a cooling agent. Financial difficulties alone stood in the way, and they were not allowed wholly to bar progress. The type of regenerative apparatus employed in 1895 being satisfactory, it was resolved to develop it on a greatly enlarged scale in a liquid-air plant, combining special arrangements for dealing with hydrogen. Its construction took a year, and many months were occupied in testing its capabilities. That they were of the high order required to compel the unconditional surrender of the gas, was at last visibly attested by the dropping of the condensed fluid into a triply-coated vacuum-vessel, May 10, 1898. By a certain dramatic fitness, the first display before an audience of this, so to speak, preternatural substance was at Professor Dewar's lecture in commemoration of the Centenary of the Royal Institution, June 7, 1899. A spheroidal vessel, silvered and vacuum-protected, containing one litre of liquid hydrogen, stood on the table, immersed in a bath of liquid air, for the *savants* of two continents to see. With these precautions, evaporation from it was not inconveniently rapid. The removal, however, of a plug of cotton-wool from the mouth of the receptacle caused an immediate deposition of *air-snow*; and the clogging of



1.—LECTURE TABLE OF THE ROYAL INSTITUTION. CENTENARY COMMEMORATION LECTURE ON LIQUID HYDROGEN.

tubes with solidified atmospheric air forms a constantly-recurring embarrassment in the use and management of liquid hydrogen.

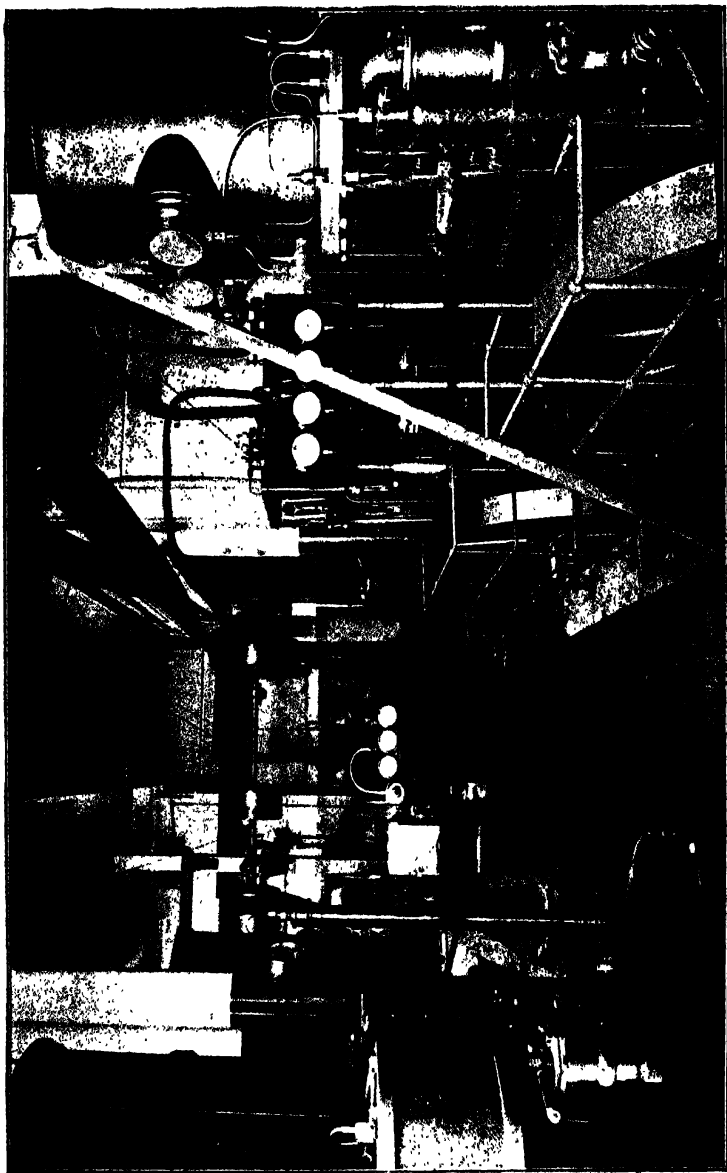
### LOW-TEMPERATURE THERMOMETERS.

This brilliant result, achieved after a long series of discouragements and failures, was only the prelude to fresh enterprises. There is no finality in science. Truth still flies before, enticing its votaries to enter upon ground more and more difficult and broken. This emphatically applies to researches on the production of artificial cold. With every downward step the obstacles become more formidable, the circumstances more critical. Even the exact determination of the temperatures attained is encompassed with difficulties. Ordinary methods of heat-measurement collapse under extraordinary conditions. Hence the choice of a thermometer for fixing the boiling-point of hydrogen was a matter of the nicest delicacy. Those giving changes of temperature in terms of electrical resistance were the most readily available; but the law of their construction, being empirical, could scarcely be expected to hold good far beyond the limit of experience. Recourse was then had to gas-thermometers of the "constant volume" form, filled severally with hydrogen, helium, oxygen, and carbonic acid. The two latter were employed to resolve the doubt whether the rule of equable contraction with cold continued valid down nearly to the boiling-points of the fiduciary substances; and they gave reassuring replies. It appeared that either a simple or a compound gas might be depended upon for the determination of temperatures until liquefaction set in. The results obtained with the hydrogen and helium thermometers might accordingly be accepted with confidence, more especially in view of their close agreement. From them it was concluded that hydrogen boils under atmospheric pressure at  $-252.5^{\circ}\text{C}$ ., or  $20.5^{\circ}$  above absolute zero; and that its critical temperature is  $-241^{\circ}\text{C}$ ., the critical pressure being about 15 atmospheres. Liquid hydrogen shows no metallic affinities. It is a non-conductor of electricity, and freezes into an ice-like solid. Its lightness is extraordinary; water is fourteen times more dense. Perfectly transparent, it gives no absorption-spectrum, and is entirely colourless. Its specific heat, although not very different from that of liquid oxygen when volumes are compared, is twelve times greater for equal weights, and is six times that of water. Its scientific value depends, however, not only upon its exceptional qualities, but upon its power as a frigorific agent. In this capacity, it was rendered serviceable only after some months of severe experience, abnormally cold substances being as troublesome to deal with as abnormally hot ones. The obstacles surmounted in the case of liquid air were presented in an aggravated form by liquid hydrogen, with the further complications due to the solidification of all the ambient air. Its preservation thus offered a twofold problem. Not only the access to it of heat had to be

hindered, but the approach of an universally diffused element. Facts learned by its use are indeed to be reckoned among the *spolia opima* of nature; they represent the trophies of an arduous conflict.

### EFFECTS OF REFRIGERATION.

Research into the effects of refrigeration is almost co-extensive with the whole realm of physics. It is concerned with the relations of matter to light, heat, electricity and magnetism. Questions as to the mode of action of cohesive and chemical forces come fully within its scope; nor is it possible to exclude from it the consideration of the intricacies of molecular structure, or even of the essential nature of material substance. These ultimate problems force themselves upon the attention of the least speculative "cryogenist." The nearer absolute zero can be approached, the more hopeful becomes the prospect of their definitive solution; and towards this "pole of cold" Professor Dewar has been pressing his way during two decades. Its actual attainment may perhaps be impossible; but the separating interval must be reduced to a minimum. The ground already won has meanwhile been carefully surveyed. Contemporaneously with unceasing efforts for the liquefaction of hydrogen, experiments were vigorously prosecuted at the temperature of liquid air. Resuming the subject of electrical resistance, Professors Dewar and Fleming carried out in 1893, and several subsequent years, an extensive series of inquiries, with more complete appliances than before for the production of refrigerating material in large quantities, with greater care in the preparation of the metallic wires submitted to trial, and with more delicate precautions in the physical measurements executed. The earlier result was confirmed that the resistivity of all pure metals falls off with increase of cold, but many abnormalities and peculiarities were brought to light. The various metals do not, in all cases, maintain the same relative places on the scale. At  $-200^{\circ}\text{C}$ . copper is a better conductor than silver, iron than zinc, aluminium than gold. The electrical eccentricities of bismuth cost the investigators protracted toil. They finally disclosed their origin from minute chemical impurities, by disappearing when electrolytic bismuth was employed. The further discovery was made that the known effect of a magnetic field in augmenting the resisting power of a bismuth wire is greatly intensified at the temperature of liquid air. That of so-called insulators, such as glass, ebonite, guttapercha, and paraffin, likewise gains as heat is subtracted. Alloys follow the opposite rule—that obeyed by pure metals—but in a half-hearted way, and with many perplexing incongruities. When liquid hydrogen was made amenable to control, it became possible to push these inquiries considerably further. At this lower depth of cold, the resistance of copper diminished to  $\frac{1}{10}$ th its efficacy at the temperature of melting ice, that of gold to  $\frac{1}{30}$ th, while  $\frac{1}{8}$ th the initial resistance of iron survived. The general upshot was besides most significant. It had been



II.—GENERAL VIEW OF REFRIGERATING MACHINERY OF THE ROYAL INSTITUTION.

logically inferred from the behaviour of pure metals down to  $-200^{\circ}\text{C}$ . that, at the absolute zero, they would entirely cease to dissipate the energy of an electric current transmitted through them. But at  $-252^{\circ}\text{C}$ ., marked inconsistencies manifested themselves. Instead of continuing their straight downward course, the resistance-curves bent round, indicating the survival, at  $0^{\circ}$  absolute, of a finite value for this property. An emphatic warning was thus conveyed against trusting to the continuity of change.

Thermo-electric action had been studied by Professor Tait at temperatures above  $0^{\circ}\text{C}$ .; the modifications produced in it by cooling down to  $-200^{\circ}\text{C}$ . were ascertained by Professors Dewar and Fleming in 1895. They present no uniform character. The curves showing the fluctuation with temperature of the thermo-electric power of various metals, do not, in all cases, even approximate to straight lines. Some—notably those of iron and bismuth—show abrupt changes of direction, indicating reversals of the “Thomson effect” at those points. Others are inflected in a manner suggestive of a zero of thermo-electric power at the zero of cold. But these indications are most likely misleading. There is every reason to believe that the rate of diminution of thermo-electric power, as of electric resistance, would fall off notably before that extreme point was reached.

Another set of experiments served to test the influence of cold upon magnetisation. They justified the expectation that magnetic moment would gain strength proportionately to the deprivation of heat. Its value was usually increased, in the fixed state established after some alterations, to the extent of thirty to fifty per cent., by lowering the temperature from  $+75^{\circ}\text{C}$ . to  $-182^{\circ}\text{C}$ . Exceptions to this rule were, however, met with. A nickel-steel magnet, for instance, is acted upon oppositely to one of carbon-steel. A subordinate result of these experiments was to show that one of the best ways of ageing a magnet is to dip it several times into liquid air. This removes sub-permanent magnetism, and induces stable relations favourable to definite observation.

The magnetic permeability of iron over a descending range of temperature was made the subject of long and laborious comparisons. They showed it to be slightly diminished by immersion in liquid oxygen. That is to say, a greater magnetic force was needed to produce a given amount of magnetisation in the cooled material. As usual, however, apparent inconsistencies were recorded. Hardened iron reversed the behaviour of soft iron. Its permeability increased at low temperatures, and, for certain values of the magnetising force, as much as five times. “Hysteresis loss,” or the dissipation of energy incidental to a cyclical process of magnetisation, was found, on the other hand, to vary little, if at all, with temperature. These diverse effects were attributed by Professor Fleming to the closer contiguity at extreme cold of the “molecular magnets,” from the collineation of which external magnetic moment results. Their groupings and

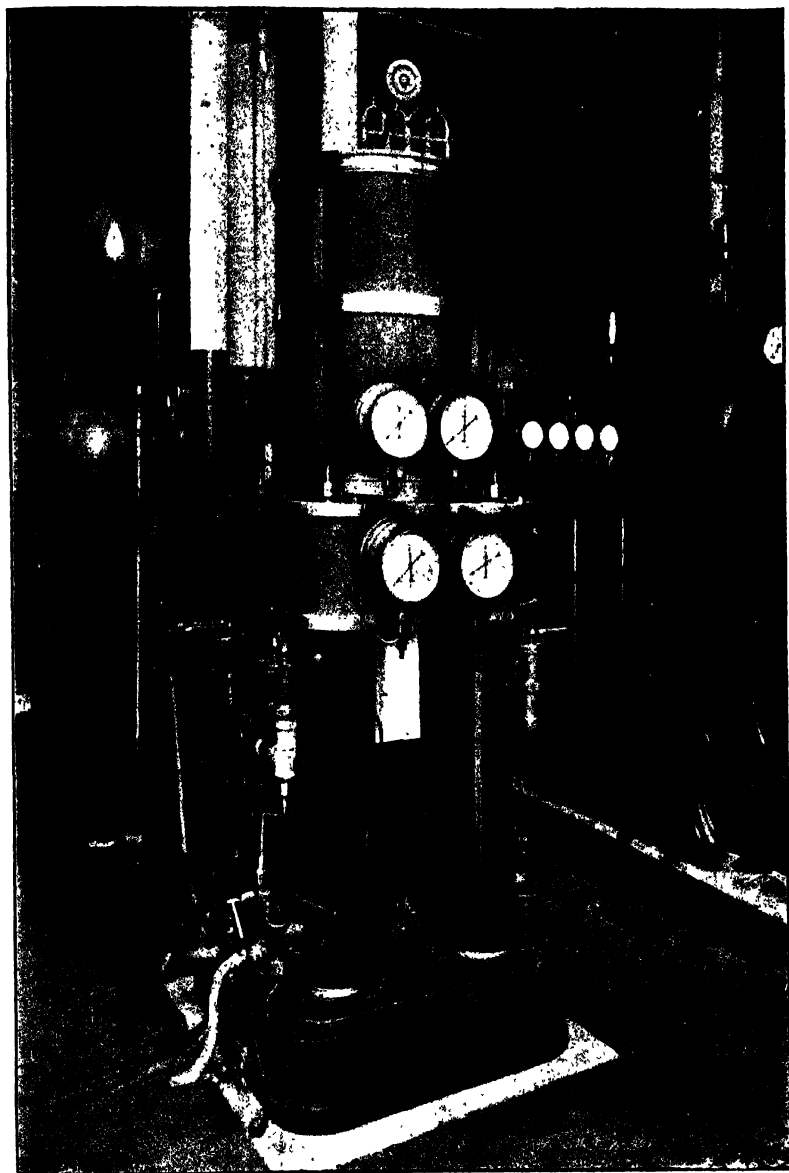
mutual action might hence undergo modifications, the intricate consequences of which can only in part be divined.

An investigation of the dielectric constants, or specific inductive capacities, of frozen electrolytes was undertaken in 1897. It met with numerous difficulties, but led to some important conclusions. These may be summarised as follows. Such substances as ice and alcohol are capable, at low temperatures, of acting as dielectrics, notwithstanding that some of them possess, in the liquid state, relatively high electrolytic conductivity. They have dielectric constants of large value near their freezing-points, which are greatly reduced by cooling down to  $-200^{\circ}\text{C}$ . At the absolute zero, these values are probably equal, all alike being two or three times that of the dielectric constant of a vacuum. Near this point, too, all electrolytes tend to acquire infinite resistivity, or to become perfect non-conductors of electricity. Finally, at very low temperatures, frozen electrolytes are nearly perfect insulators, but they rapidly regain sensible conducting power at temperatures far below their melting-points.

Oxygen and air in the liquid state were inferred from their remarkable insulating quality to be dielectrics; and it was accordingly desirable to ascertain their dielectric constants, in terms of that of a vacuum taken as unity. They came out 1.493 and 1.495 respectively. Between the magnetic susceptibility of gaseous and liquid oxygen a significant difference was elicited. The ratio for equal volumes proved to be 1594 to 1. The magnetic susceptibility, in other words, of the gas was, for equal masses, nearly doubled by liquefaction; whence the inference was drawn that this property does not simply appertain to "the molecule *per se*, but is a function of the state of aggregation." Noteworthy, besides, was the verification for liquid oxygen of Maxwell's law connecting magnetic permeability, specific inductive capacity, and optical refractivity. Additional experiments on liquid oxygen made in 1898, on a different principle from that previously adopted, afforded a qualified confirmation to the law that magnetic susceptibility varies directly as the density of the paramagnetic body, and inversely as its absolute temperature.

So far from showing any tendency to disintegrate into "cosmic dust," matter grows continually more rigid with cooling. A metallic rod will sustain, for the same extension, four or five times the weight at  $-182^{\circ}$  that it would at  $0^{\circ}\text{C}$ . A coil of fusible metal wire, which the tension of a single ounce would pull out straight at the ordinary temperature, will support a couple of pounds and vibrate like a steel spring after immersion in liquid air. The most definite means, however, of determining the changes in cohesive force produced by cold, is to compare the breaking stresses of metals at moderate and very low temperatures. The necessary experiments, it is true, involve the expenditure of gallons of frigid and costly fluids; they were, nevertheless, carried out satisfactorily at the Royal Institution in 1893. They showed a large increase with cooling in the tenacity of all common metals and alloys. Exceptions presented by castings of zinc,





III.—LIQUID HYDROGEN APPARATUS OF THE ROYAL INSTITUTION.

bismuth and antimony, were almost certainly more apparent than real; an explanation of them lay ready to hand in the crystalline structure of these bodies, the internal strains occasioned in which by extreme lowering of temperature, would naturally result in the weakening of some set of cleavage-planes, and comparatively easy rupture. Measurements of the elastic constant known as the "Young modulus," showed that it increased between four and five times by cooling from  $+15^{\circ}\text{C.}$  to  $-182^{\circ}$ , and balls of iron, tin, lead or ivory, rebounded much higher after the same treatment when dropped from a fixed height upon an iron anvil. The general outcome was to make it clear that cohesion gains effectiveness with added contiguity of the particles acted upon, in this resembling gravitation. Professor Dewar's experiments with liquid air thus lent countenance to Lord Kelvin's view that gravitation is adequate to account for cohesion.

They also disclosed marked alterations, at low temperatures, in the optical properties of certain bodies. Changes of colour, corresponding to changes in the specific absorption of light, were at once obvious. Vermilion and mercuric iodide paled from brilliant scarlet to faint orange; nitrate of uranium and the double chloride of platinum and ammonium turned white—the original hue returning in all cases with the restoration of warmth. Blues, however, remain unaffected by cold, and organic dyes are but slightly sensitive to it.

Temperature has long been known to play an important part in the phenomena of phosphorescence; their study, accordingly, under the intensely frigid conditions realised by Professor Dewar's work in liquefying intractable gases, seemed desirable. It yielded a variety of most interesting facts. On the whole, bodies gain greatly in phosphorescent capability by cooling to  $-182^{\circ}\text{C.}$  Gelatin, celluloid, paraffin, ivory, horn, indiarubber—in all of which the quality is ordinarily inconspicuous—omit a bluish luminosity, on being stimulated by the electric light, after immersion in liquid oxygen. Alkaloids forming fluorescent solutions invariably become phosphorescent at low temperatures. Glycerin, sulphuric, nitric and hydrochloric acids, and strong ammonia, are also very bright, as well as most substances containing a ketone group. Milk is highly phosphorescent, pure water but slightly so. An egg shone as a globe of blue light; and striking effects were obtained from many other organic products—from feathers, cotton-wool, tortoiseshell, paper, leather, linon, sponge, besides some species of white flowers; above all, from white of egg, which, with proper management, became vividly self-luminous. Complexity of structure was inferred to be one of the main conditions upon which the possession of this quality depends. The discovery that it belongs to oxygen alone among simple gases was accordingly unexpected. A current of oxygen flowing into an exhausted tube, after exposure to an electric spark, emits hazy white light, and the attendant formation of ozone attests the simultaneous progress of molecular change. The effect is completely stopped by the presence of hydrogen, or by the least trace of organic matter. At the tempera-

ture of liquid hydrogen, phosphorescent action is still further intensified; it may, although exceptionally, even at  $-250^{\circ}$  C. be set on foot by light deprived of its ultra-violet rays.

The electric stimulation of crystals by cooling brings about actual discharges between the molecules. In some platino-cyanides and in nitrate of uranium, the temperature of liquid air suffices to develop marked electrical and luminous phenomena, which are intensified and extended through the agency of liquid hydrogen. The importance of a systematic study of pyro-electricity under such conditions was pointed out by Professor Dewar in the Bakerian Lecture delivered June 13, 1901.

Chemical affinity is almost completely abolished by cold. Phosphorus, sodium, potassium, remain inert in liquid oxygen; and voltaic combinations, brought down to its temperature, cease to give electric currents. Photographic films, however, retain about one-fifth of their ordinary sensitiveness to light, nor does it wholly disappear even through the agency of liquid hydrogen. Possibly the decomposing force which comes into play under these circumstances is not chemical, but mechanical; if so, no trace of photographic action would be apparent were it possible to carry out development under the frigid conditions of exposure.

An elaborate course of experiments on thermal transparency, carried out in 1897-8, completely negatived Pictet's conclusion that, at a given degree of cold, non-conducting substances lose their faculty of insulation. They were proved to retain it unimpaired at the boiling-point of air, the abnormal transferences of heat observed at Geneva having been due, not so much to the materials themselves, as to the air contained in their interstices. The utility was thus rendered apparent of investigating problems of heat-transmission with the aid of liquid air. The comparative absorption of Röntgen-rays by various frigid bodies formed about the same time a subject of inquiry; and the view that the atomic weight of argon is double its density relative to hydrogen, obtained confirmation from the approximately equal opacities found for that substance in the liquid state, for liquid chlorine, and for potassium. This was the first use of the Röntgen radiation for the purpose of defining atomic weight.

#### LIQUEFACTION OF FLUORINE.

The liquefaction of fluorine preceded by one year the liquefaction of hydrogen. That this peculiar substance would prove highly recalcitrant to condensation had long been known by sure indications derived from the character of its compounds. Thus, while chloride of ethyl boils at  $+12^{\circ}$  C., fluoride of ethyl boils only at  $-32^{\circ}$ ; and similarly, the boiling points of chloride and fluoride of propyl are respectively  $+45^{\circ}$  and  $-2^{\circ}$ . Analogous values for the same constant are given by the various inorganic haloid compounds. The obstinate gaseity of fluorine was at length overcome through a com-

bination of forces. M. Moissan, a specialist in the practical chemistry of the element, brought his apparatus for its production to the Royal Institution, for the purposes of his lecture, on May 28, 1897, and it was used next day, in connexion with Professor Dewar's refrigerating plant, to obtain the first specimen of liquid fluorine. This is a clear yellow fluid of great mobility, boiling in open vessels at  $-187^{\circ}\text{C.}$ , and refusing to solidify at  $-210^{\circ}$ . The following are its chief ascertained properties. It is soluble in liquid air and oxygen; its density is 1.14 that of water; it has a capillarity less than that of liquid hydrogen; it gives no absorption-spectrum, and is devoid of magnetic quality. The energetic chemical affinities characteristic of the gas are almost entirely suppressed by the extreme cold needed for its condensation. The liquid rests harmlessly in glass bulbs; it is indifferent to oxygen, water or mercury; only hydrogen and hydrocarbons excite it to reaction with incandescence.

#### SOLID HYDROGEN, OXYGEN, AND AIR.

The freezing of atmospheric air was first accomplished by Professor Dewar in 1893. A litre of liquid air, subjected to exhaustion in a silvered vacuum-vessel, yields about half that volume of colourless, transparent solid, which may last as such for half an hour. Under magnetic compulsion, liquid oxygen is drawn to the poles from the meshes of the "nitrogen-jelly," which forms the really solid part of air-ice. This substance can only be examined in a vacuum or in an atmosphere of hydrogen, since it instantly melts in contact with the atmosphere, giving rise, at the same time, to a further liquefaction of air. The interaction of the two processes can be watched, and is curious to discriminate. The difference between the conditions of freezing of oxygen and nitrogen depends upon the circumstance that the vapour-pressure of the former substance, boiling in an exhausted receiver, is inappreciable; that of the latter, quite considerable. Solid oxygen can only be obtained through the agency of liquid hydrogen. It is clear, blue ice. Hydrogen itself was solidified by Professor Dewar, not without much difficulty, in 1899. This final product of refrigeration has a fusing-point of about  $15^{\circ}$  absolute, at a vapour-pressure of 55 millimetres. It has the appearance of perfectly pure ice; there is nothing metallic about it. The exhibition to a crowded audience in the theatre of the Royal Institution, April 6, 1900, of a form of matter representing so much victorious exertion was a triumph tempered by the reflection that the hydrogen-route towards the absolute zero stopped with its production, leaving a trackless interval of narrow extent, but immense importance.

The era of "new gases" began in 1894, with the isolation of argon; helium was shortly afterwards extracted from cleveite and other rare minerals; krypton, neon, and xenon were in 1898 spectroscopically identified as atmospheric constituents by Professor

Ramsay and Dr. Travers, using the method of fractionation at low temperatures. These successive discoveries suggested new and unexpected problems, and offered fresh opportunities for pioneering research. Argon, indeed, condenses with what may now be reckoned as tolerable facility. M. Olszewski reduced a sample of gas sent him by Professor Ramsay in 1895, to a colourless liquid, boiling under atmospheric pressure at  $-187^{\circ}\text{C}$ ., and one-and-a-half times denser than water. It freezes into a transparent, glassy solid near  $-190^{\circ}\text{C}$ . Helium, on the other hand, is more volatile than hydrogen. Its liquefaction will accordingly give a lower temperature—*will give*, for it has not yet been accomplished. This strange and rare ingredient of our planet is the one accessible substance which remained invincibly gaseous at the close of the nineteenth century; there is no reason to doubt, however, that liquid helium will, in the twentieth, form one of the earliest trophies of research. Lord Kelvin's forecast of a substance by means of which the distance to absolute zero would be abridged from  $15^{\circ}$  to  $5^{\circ}$ , may then be realised.

#### INERT COMPONENTS OF ATMOSPHERIC AIR.

The "inert" components of air may be ranked as a distinct class of bodies. They combine several exceptional peculiarities. They resemble mercury in being monatomic; the physical unit or molecule, is identical with the chemical unit, misnamed an atom; hence their density, as compared with hydrogen, is half their atomic weight. They stand apart from all other known substances in being devoid of chemical affinities; to a very limited extent they are capable of being dissolved by certain liquids, and absorbed by certain minerals; but they are strictly "non-valent"; they form no true compounds. For this reason, and because of the minute proportions in which they occur, ordinary tests fail to disclose their presence. They have no visible function in nature; they exist as if by a survival of an earlier order of things; their appointed part was perhaps played while the earth was still in the nebulous stage. They are wonderfully volatile considering their densities, and for this reason are of especial interest to cryogenists. The following little table gives the densities and boiling-points, according to Ramsay and Travers, of the five members of the group so far recognised:—

Element.	Density.	Atomic Weight.	Boiling-Point (Centigrade).
Helium .. .. .	1.98	3.96	below $-262^{\circ}$
Neon .. .. .	about 10.0	about 20	about $-239^{\circ}$
Argon .. .. .	19.96	39.92	$-187^{\circ}$
Krypton .. .. .	40.88	81.76	$-152^{\circ}$
Xenon .. .. .	• 64	128	$-109^{\circ}$

Lord Rayleigh showed that the refractivity of helium was very small, being only 0.1238. On the same scale (refractivity of air = 1.0), the value of the constant for hydrogen is 0.469, or nearly four times greater, the opposite disparity of densities notwithstanding. The monatomic constitution of all these gases was established by finding 1.66 as the ratio between their specific heats at constant pressure and at constant volume. While exercising no appreciable absorption upon light, they glow brilliantly through the action of an electric discharge. An excited neon-tube flames with an orange-pink colour; krypton shines pale violet; xenon luminesces in sky-blue. The corresponding spectra are extremely vivid and characteristic. The progress of research at low temperatures led to anticipatory partial disclosures of them. In a paper 'On the Spectra of the Electric Discharge in Liquid Oxygen, Air and Nitrogen,' published in 1894 in the *Philosophical Magazine*, Professors Livoing and Dewar recorded the appearance, during the distillation and concentration *in vacuo* of liquid oxygen and air under diminished pressure, of two unknown bright lines at wave-lengths 557 and 555, the former coinciding approximately with the chief auroral ray. Both were subsequently, by Professor Ramsay and Dr. Travers, associated with krypton. Again, some strange bright lines, belonging to the then unidentified spectrum of neon, were derived by Professor Dewar in 1897 from a vacuum-tube filled with a residuum of gas from the King's Well at Bath, collected by the kind permission of the Corporation of that town; this is one of the most valuable among the available sources for the supply of scarce aerial constituents.

#### LOW TEMPERATURE AS AN ANALYTIC AGENT.

What may almost be designated a new branch of pneumatic chemistry, the analysis of gases by cold, was set on foot by Professor Dewar in 1897. On the 4th of November in that year, he described before the Chemical Society an apparatus for determining the proportion of any atmospheric ingredient that remains uncondensed at  $-210^{\circ}$  C. and is insoluble in liquid air under standard pressure. Preliminary experiments showed that one part of hydrogen in a thousand of air could just be detected by the newly devised method, and that liquid air can dissolve one-fifth of its own volume of hydrogen. Helium proved to be soluble, though in a less degree, in liquid nitrogen. With the powerful aid of liquid hydrogen, these researches were continued during four ensuing years. A striking illustration of its extraordinary effectiveness in refrigeration is afforded by the rapid production, through its means, of high vacua. It was computed that the pressure of air in sealed tubes, frozen out by immersion in liquid hydrogen, could not exceed one-millionth of an atmosphere, apart from any that might result from the survival, in minute quantities, of gases more refractory than oxygen or nitrogen. The exhaustion, in other words, due to the frigorific treatment of air-

bulbs, is theoretically about the same obtained by boiling out a space with mercury. Practically, it turned out to be even higher. In carefully prepared tubes, vacua so nearly perfect were produced that heat had to be applied before a spark could be got to pass. Their spectroscopic examination gave results of singular interest. Carbonic oxide bands were generally present, but might be traced to emanations from the glass; they were associated with lines of hydrogen and helium, and the distinctive yellow ray of neon. The path thus struck out was pursued further in August 1900, when, by an improved process, some tubes were filled at low pressure with the more volatile gases of the atmosphere. Traces of nitrogen, argon, and carbon-compounds, having been abolished by a bath of liquid hydrogen, sparking brought out prominently the spectra of hydrogen, helium, and neon, together with a number of less brilliant rays of unknown origin. Excited by continuous electric discharges, tubes thus prepared glow throughout with a strong orange light. The violet and ultra-violet sections of the spectrum given by it seem, nevertheless, to rival the strength of its red and yellow rays, so far as could be judged from spectrographic evidence. Sensitive plates received impressions of great intensity up to a wave-length of 314, despite the opacity of glass to such rapid vibrations. The photographs, it is true, were taken with a quartz calcite train, but there was still the glass of the tubes to be reckoned with.

The wave-lengths of nearly three hundred rays in the spectrum derived in this manner from residual atmospheric gases, uncondensed at the temperature of liquid hydrogen, were measured by Professors Liveing and Dewar, the spark-spectrum of iron serving for a standard of reference. Of these, 69 were identified, certainly or probably, as emanating from hydrogen, helium or neon, and it was noted, as a fact of no small significance, that among them were four members of the ultra-violet hydrogen series. For, under ordinary circumstances, they are omitted only by gas carefully purified; yet here they emerged with comparative facility on plates exposed to light from a heterogeneous mixture. An unexpected hint is thus afforded regarding the conditions that may tend to modify the hydrogen-spectrum in passing from star to star. Coincidences were diligently sought among the unknown lines with nebular, coronal and auroral rays, but with dubious or partial success. The possibility, however, was not excluded that "nebulum" might actually lurk, almost infinitesimally, in the earth's atmosphere, since, from one tube which, owing to its somewhat different treatment, preserved traces of nitrogen and argon, a faint additional ray was derived, agreeing approximately in position with the chief bright line of gaseous nebulae at  $\lambda$  5007. Further observations were contemplated for the verification of this curiously interesting suggestion. A good many subordinate lines in the tube-spectra fell very near the places assigned to radiations from the sun's corona; yet here, again, confirmation was needed before the terrestrial presence of coronium

could be regarded as even probable. Instances of agreement with the auroral spectrum were also adverted to; and some are likely to prove genuine. In this direction, certainly, lies the best hope of elucidating the baffling problem of the "Northern Lights."

By the use of liquid hydrogen as an analytic agent, neon can be spectroscopically distinguished through its yellow line at  $\lambda$  5853, in 25 cubic centimetres of ordinary air. The searching nature of the method may be estimated from the consideration that the proportion of the gas present is only one in 40,000. The fundamental neon-line, indeed, predominates in the spectrum of the atmospheric residuum, very much as the adjacent ray of helium does in the prismatic light emanating from the more volatile portion of the Bath gas. Both rays shine in each spectrum, but with reversed brilliancy. Professor Dewar's inquiries thus confirmed the status of helium as an invariable atmospheric constituent. They, moreover, demonstrated the association with it of hydrogen. In every sample of air there is a percentage of hydrogen. The ratio by volume, according to M. Armand Gautier's recent determination, is 1 to 5000. If, then, as Dr. Johnstone Stoney maintains, the velocities of its molecules are, in the long run, uncontrollable by gravity, the leakage thence ensuing must be compensated either from within or from without. Subterranean sources perhaps supply the deficit; or interplanetary space itself gives back as many vagrant molecules as it receives. A balance, at any rate, is evidently struck somehow.

In a later communication to the Royal Society (read June 20, 1901), Professors Liveing and Dewar dealt with the least volatile, as they had previously dealt with the most volatile of the atmospheric gases. Separated from liquid air by careful processes of distillation, xenon and krypton were submitted to spectroscopic examination, in the course of which the variations of their spectra with the character of the electric discharge attracted particular attention. The rays of xenon measured and tabulated numbered 257, those of krypton, 182.

#### LOW TEMPERATURE AND VITAL PHENOMENA.

Low-temperature research is of extreme importance to the study of vital phenomena. Our ideas as to the nature of life, and our conjectures regarding the course of its history on this planet, must be largely regulated by experience of its capability to resist extremes of heat and cold. Now the upper limit of endurance is easily reached; it is never above, and is usually considerably below  $+100^{\circ}\text{C.}$ ; but germicidal cold has not yet been produced. Warm-blooded animals, to be sure, necessarily perish, and perish promptly, under frigid conditions. The power of resistance, however, increases with simplicity of organisation; and the ultimate atoms of life (so to call bacteria) bear with impunity an indefinite amount and degree of freezing. Professor M'Kendrick found, in 1893, that sterilisation did not result from an hour's exposure to a temperature of  $-182^{\circ}\text{C.}$  Samples of



blood, meat and milk, sealed in glass tubes, underwent putrefaction in the ordinary course after prolonged immersion in liquid oxygen. Nor was the germinating power of seeds impaired by subjection to the ordeal. Seven years later, Dr. Allan Macfadyen carried out an extensive series of experiments of this nature at the Royal Institution, under the personal supervision of Professor Dewar. The action of liquid air on bacteria was first tested. It proved entirely innocuous. After twenty hours at  $-190^{\circ}\text{C.}$ , no diminution in their powers of growth, or in any of their functional activities, was perceptible. Phosphorescent organisms supplied a striking illustration of the alternate suspension and renewal of vital processes by freezing and thawing. Cooled down in liquid air they become non-luminous, but the intra-cellular oxidation producing the phosphorescence recommenced with full vigour when the temperature was raised. The sudden cessation and rapid renewal of the shining faculty of the cells, despite extreme changes of temperature, were eminently instructive. Seven days in liquid air proved no more deleterious to bacterial life than twenty hours. The temperature of liquid hydrogen was tried, with the same upshot; the much-enduring series of organisms dealt with suffered no injury. At  $21^{\circ}$  absolute, then, and probably much nearer to the zero-point, life can continue to exist. It can continue to exist, that is to say, under conditions bringing about an entire cessation of chemical, and an approximate cessation of molecular, activity. These facts, as Dr. Macfadyen remarked, "afford new ground for reflection as to whether life, after all, is dependent for its continuance on chemical reactions." Biologists, he added, "therefore follow with the keenest interest Professor Dewar's heroic attempts to reach the absolute zero"; while his success so far has already thrown open to them a new realm of experimentation, and placed in their hands an agent of investigation from the effective use of which they may "hope to gain a little further insight into the great mystery of life itself." The speculative interest of these researches supplies, indeed, the keenest incentive to their prosecution. The transmissibility from planet to planet, for instance, of living germs or spores has often been debated; it is now known that the cold of space would be unlikely to stand in the way. There are, however, other difficulties less easily removable; nor, even if a cosmic community of bacterial species were established, should we find ourselves any nearer to the heart of the creative mystery of life's origin.

The development of low-temperature chemistry is one of the most striking features of scientific history during the last decade of the nineteenth century. Many questions of profound interest have been answered through its means, and a partial insight has been gained into some of the most recondite secrets of nature. The unique condition attends it, that the *ne plus ultra* cannot recede as it advances. The absolute zero forms an irremovable landmark, a boundary-line that may not be transgressed, an asymptote, as it were, to the curve of future progress. And every step nearer to it is

harder to take than the previous one. Among many causes of augmenting difficulty is the circumstance that the molecular latent heats of vaporisation diminish with the absolute boiling-point. Hence, a continually more lavish expenditure of frigorific material is necessitated, and of material the price of which, in money and labour, rises rapidly with its frigorific efficacy. Still, although the bottom of the temperature-scale may never be actually reached, the intervening space will surely be much abridged. But we shall never, it is safe to predict, assist at the "death of matter." At the stage arrived at, there is no sign of its being moribund. Forces still act within and upon it. Gravity and cohesion maintain their normal power. It sensibly impedes the passage of electricity in the purest and most highly conducting metals. Its minute particles can take up and modify luminous vibrations. Only chemical affinity seems to be extinct; the various species of matter cease to react upon each other. The next cryogenic achievement, it is true, may alter the situation as we now see it. Our present standing-ground may be subverted, for the inquiry is just now in a critical phase. The liquefaction of helium, for example, may prove decisive of many things—it may set at rest some doubts, and raise unlooked-for issues.

The conditions for its accomplishment were clearly set forth in the Bakerian Lecture. They may be realised by the use of methods actually available. This last fortress of gasceity cannot be regarded as impregnable, although its capture will be at a high monetary cost. Gaseous helium, to begin with, is of the utmost scarcity; and what is scarce demands outlay to procure. Its condensation can be effected only by subjecting it to the same process that succeeds with hydrogen, substituting, however, liquid hydrogen under exhaustion for liquid air as the primary cooling agent. As the upshot, a liquid will be at hand, boiling at about  $5^{\circ}$  absolute, or  $-268^{\circ}$  C., but more expensive than liquid hydrogen, in a much higher ratio than liquid hydrogen is more expensive than liquid air. By comparison, "potable gold" would be a cheap fluid. Nor could the precious metal, in that, or any other form, be employed for a higher intellectual purpose than in promoting and extending researches of such boundless promise and commanding interest as those conducted at the Royal Institution.

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Friday, January 17, 1902.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.O.L. F.R.S.,  
President, in the Chair.

THE RIGHT HON. LORD RAYLEIGH, M.A. D.C.L. LL.D. Sc.D.  
F.R.S. M.R.I., Professor of Natural Philosophy, R.I.

*Interference of Sound.*

For the purposes of laboratory or lecture experiments it is convenient to use a pitch so high that the sounds are nearly or altogether inaudible. The wave lengths (1 to 3 cm.) are then tolerably small, and it becomes possible to imitate many interesting optical phenomena. The ear as the percipient is replaced by the high pressure sensitive flame, introduced for this purpose by Tyndall, with the advantage that the effects are visible to a large audience.

As a source of sound a "bird-call" is usually convenient. A stream of air from a circular hole in a thin plate impinges centrically upon a similar hole in a parallel plate held at a little distance. Bird-calls are very easily made. The first plate, of 1 or 2 cm. in diameter, is cemented, or soldered, to the end of a short supply-tube. The second plate may conveniently be made triangular, the turned down corners being soldered to the first plate. For calls of medium pitch the holes may be made in tin plate. They may be as small as  $\frac{1}{2}$  mm. in diameter, and the distance between them as little as 1 mm. In any case the edges of the holes should be sharp and clean. There is no difficulty in obtaining wave-lengths (complete) as low as 1 cm., and with care wave-lengths of .6 cm. may be reached, corresponding to about 50,000 vibrations per second. In experimenting upon minimum wave-lengths, the distance between the call and the flame should not exceed 50 cm., and the flame should be adjusted to the verge of flaring.\* As most bird-calls are very dependent upon the precise pressure of the wind, a manometer in immediate connection is practically a necessity. The pressure, originally somewhat in excess, may be controlled by a screw pinch-cock operating on a rubber connecting tube.

In the experiments with conical horns or trumpets, it is important that no sound should issue except through these channels. The horns end in short lengths of brass tubing which fit tightly to a short length of tubing (A) soldered air-tight on the face of the front

\* 'Theory of Sound,' 2nd ed., § 371.

plate of the bird-call. So far there is no difficulty ; but if the space between the plates be boxed in air-tight, the action of the call is interfered with. To meet this objection a tin-plate box is soldered air-tight to A, and is stuffed with cotton-wool kept in position by a *loosely* fitting lid at C. In this way very little sound can escape except through the tube A, and yet the call speaks much as usual. The manometer is connected at the side tube D. The wind is best supplied from a gas-holder.

With the steadily maintained sound of the bird-call there is no difficulty in measuring accurately the wave-lengths by the method of nodes and loops. A glass plate behind the flame, and mounted so as to be capable of sliding backwards and forwards, serves as reflecting wall. At the plate, and at any distance from it measured by an

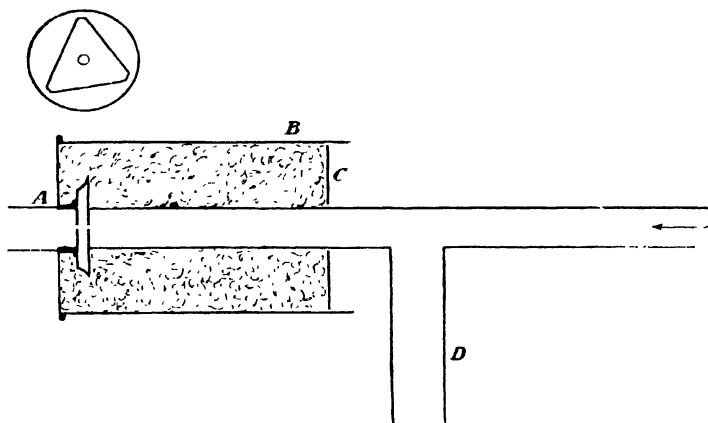


FIG. 1.

even number of quarter wave-lengths there are nodes, where the flame does not respond. At intermediate distances, equal to *odd* multiples of the quarter wave-length, the effect upon the flame is a maximum. For the present purpose it is best to use nodes, so adjusting the sensitiveness of the flame that it only just recovers its height at the minimum. The movement of the screen required to pass over ten intervals from minimum to minimum may be measured, and gives at once the length of five complete progressive waves. For the bird-call used in the experiments of this lecture the wave length is 2 cm. very nearly.

When the sound whose wave length is required is not maintained, the application of the method is, of course, more difficult. Nevertheless, results of considerable accuracy may be arrived at. A steel bar, about 22 cm. long, was so mounted as to be struck longitudinally

every two or three seconds by a small hammer. Although in every position the flame shows some uneasiness at the stroke of the hammer, the distinction of loops and nodes is perfectly evident, and the measurement of wave length can be effected with an accuracy of about 1 per cent. In the actual experiment the wave length was nearly 3 cm.

The formation of stationary waves with nodes and loops by perpendicular reflection illustrates interference to a certain extent, but for the full development of the phenomenon the interfering sounds should be travelling in the same, or nearly the same, direction. The next example illustrates the theory of Huyghens' zones. Between the bird-call and the flame is placed a glass screen perforated with a circular hole. The size of the hole, the distances, and the wave length are so related to one another that the aperture just includes the first and second zones. The operation of the sounds passing these zones is antagonistic, and the flame shows no response until a part of the aperture is blocked off. The part blocked off may be either the central circle or the annular region defined as the second zone. In either case the flame flares, affording complete proof of interference of the parts of the sound transmitted by the aperture.

From a practical point of view the passage of sound through apertures in walls is not of importance, but similar considerations apply to its issue from the mouths of horns, at least when the diameter of the mouth exceeds the half wave-length. The various parts of the sound are approximately in the same phase when they leave the aperture, but the effect upon an observer depends upon the phases of the sounds, not as they leave, but as they arrive. If one part has further to go than another, a phase discrepancy sets in. To a point in the axis of the horn, supposed to be directed horizontally, the distances to be travelled are the same, so that here the full effect is produced, but in oblique directions it is otherwise. When the obliquity is such that the nearest and furthest parts of the mouth differ in distance by rather more than one complete wave-length, the sound may disappear altogether through antagonism of equal and opposite effects. In practice the attainment of a complete silence would be interfered with by reflections, and in many cases by a composite character of sound, viz. by the simultaneous occurrence of more than one wave-length.

In the fog-signals established on our coasts the sound of powerful sirens issues from conical horns of circular cross-section. The influence of obliquity is usually very marked. When the sound is observed from a sufficient distance at sea, a deviation of even  $20^{\circ}$  from the axial line entails a considerable loss, to be further increased as the deviation rises to  $40^{\circ}$  or  $60^{\circ}$ . The difficulty thence arising is met, in the practice of the Trinity House, by the use of two distinct sirens and horns, the axes of the latter being inclined to one another at  $120^{\circ}$ . In this way an arc of  $180^{\circ}$  or more can be efficiently



guarded, but a more equable distribution of the sound from a single horn remains a desideratum.

Guided by the considerations already explained, I ventured to recommend to the Trinity House the construction of horns of novel design, in which an attempt should be made to spread the sound out horizontally over the sea, and to prevent so much of it from being lost in an upward direction. The solution of the problem is found in a departure from the usual circular section, and the substitution of an elliptical or elongated section, of which the short diameter, placed horizontally, does not exceed the half wave-length; while the long diameter, placed vertically, may amount to two wave-lengths or more. Obliquity in the *horizontal plane* does not now entail much difference of phase, but when the horizontal plane is departed from such differences enter rapidly.

Horns upon this principle were constructed under the supervision of Mr. Matthews, and were tried in the course of the recent experiments off St. Catherine's. The results were considered promising, but want of time and the numerous obstacles which beset large-scale operations prevented an exhaustive examination.

On a laboratory scale there is no difficulty in illustrating the action of the elliptical horns. They may be made of thin sheet brass. In one case the total length is 20 cm., while the dimensions of the mouth are 5 cm. for the long diameter and  $1\frac{1}{4}$  cm. for the shorter diameter. The horn is fitted at its narrow end to A (Fig. 1), and can rotate about the common horizontal axis. When this axis is pointed directly at the flame, flaring ensues; and the rotation of the horn has no visible effect. If now, while the long diameter of the section remains vertical, the axis be slewed round in the horizontal plane until the obliquity reaches  $50^\circ$  or  $60^\circ$ , there is no important falling off in the response of the flame. But if at obliquities exceeding  $20^\circ$  or  $30^\circ$  the horn is rotated through a right angle, so as to bring the long diameter horizontal, the flame recovers as if the horn had ceased sounding. The fact that there is really no falling off may be verified with the aid of a reflector, by which the sound proceeding at first in the direction of the axis may be sent towards the flame.

When the obliquity is  $60^\circ$  or  $70^\circ$  it is of great interest to observe how moderate a departure from the vertical adjustment of the longer diameter causes a cessation of effect. The influence of maladjustment is shown even more strikingly in the case of a larger horn. According to theory and observation a serious falling off commences when the tilt is such that the difference of distances from the flame of the two extremities of the long diameter reaches the half wave length—in this case 1 cm. It is thus abundantly proved that the sound issuing from the properly adjusted elliptical cone is confined to a comparatively narrow belt round the horizontal plane and that in this plane it covers efficiently an arc of  $150^\circ$  or  $160^\circ$ .

Another experiment, very easily executed with the apparatus

already described, illustrates what are known in Optics as Lloyd's bands. These bands are formed by the interference of the direct vibration with its very oblique reflection. If the bird-call is pointed toward the flame, flaring ensues. It is only necessary to hold a long board horizontally under the direct line to obtain a reflection. The effect depends upon the precise height at which the board is held. In some positions the direct and reflected vibrations co-operate at the flame and the flaring is more pronounced than when the board is away. In other positions the waves are antagonistic and the flame recovers as if no sound were reaching it at all. This experiment was made many years ago by Tyndall who instituted it in order to explain the very puzzling phenomenon of the "silent area." In listening to fog-signals from the sea it is not unfrequently found that the signal is lost at a distance of a mile or two and recovered at a greater distance in the same direction. During the recent experiments the Committee of the Elder Brethren of the Trinity House had several opportunities of making this observation. That the surface of the sea must act in the manner supposed by Tyndall cannot be doubted, but there are two difficulties in the way of accepting the simple explanation as complete. According to it the interference should always be the same, which is certainly not the case. Usually there is no silent area. Again, although according to the analogy of Lloyd's bands there might be a dark or silent place at a particular height above the water, say on the bridge of the *Irene*, the effect should be limited to the neighbourhood of the particular height. At a height above the water twice as great, or near the water level itself, the sound should be heard again. In the latter case there were some difficulties, arising from disturbing noises, in making a satisfactory trial; but as a matter of fact, neither by an observer up the mast nor by one near the water level, was a sound lost on the bridge ever recovered.

The interference bands of Fresnel's experiment may be imitated by a bifurcation of the sound issuing from A (Fig. 1). For this purpose a sort of T-tube is fitted, the free ends being provided with small elliptical cones, similar to that already described, whose axes are parallel and distant from another by about 40 cm. The whole is constructed with regard to symmetry, so that sounds of equal intensity and of the same phase issue from the two cones whose long diameters are vertical. If the distances of the burner from the mouths of the cones be precisely equal, the sounds arrive in the same phase and the flame flares vigorously. If, as by the hand held between, one of the sounds is cut off, the flaring is reduced, showing that with this adjustment the two sounds are more powerful than one. By an almost imperceptible slewing round of the apparatus on its base-board the adjustment above spoken of is upset and the flame is induced to recover its tall equilibrium condition. The sounds now reach the flame in opposition of phase and practically neutralise one another. That this is so is proved in a moment. If the hand be introduced

between either orifice and the flame, flaring ensues, the sound not intercepted being free to produce its proper effect.

The analogy with Fresnel's bands would be most complete if we kept the sources of sound at rest and caused the burner to move transversely so as to occupy in succession places of maximum and minimum effect. It is more convenient with our apparatus and comes to the same thing, if we keep the burner fixed and move the sources transversely, sliding the base-board without rotation. In this way we may verify the formula, connecting the width of a band with the wave-length and the other geometrical data of the experiment.

The phase discrepancy necessary for interference may be introduced, without disturbing the equality of distances, by inserting in the path of one of the sounds a layer of gas having different acoustical properties from air. In the lecture carbonic acid was employed. This gas is about half as heavy again as air, so that the velocity of sound is less in the proportion of  $1:1.25$ . If  $l$  be the thickness of the layer, the *retardation* is  $.25l$ ; and if this be equal to the half wave-length, the interposition of the layer causes a transition from complete agreement to complete opposition of phase. Two cells of tin plate were employed, fitted with tubes above and below, and closed with films of collodion. The films most convenient for this purpose are those formed upon water by the evaporation of a few drops of a solution of celluloid in pear-oil. These cells were placed one in the path of each sound, and the distances of the cones adjusted to maximum flaring. The insertion of carbonic acid into *one* cell quieted the flame, which flared again when the second cell was charged so as to restore symmetry. Similar effects were produced as the gas was allowed to run out at the lower tubes, so as to be replaced by air entering above.\*

Many vibrating bodies give rise to sounds which are powerful in some directions but fail in others—a phenomenon that may be regarded as due to interference. The case of tuning forks (unmounted) is well known. In the lecture a small and thick wine-glass was vibrated, after the manner of a bell, with the aid of a violin bow. When any one of the four vibrating segments was presented to the flame, flaring ensued; but the response failed when the glass was so held at the same distance that its *axis* pointed to the flame. In this position the effects of adjacent segments neutralise one another and the aggregate is zero. Another example, which, strangely enough, does not appear to have been noticed, is afforded by the familiar open organ pipe. The vibrations issuing from the two ends are in the same phase as they start, so that if the two ends are equally distant from the percipient, the effects conspire. If, however, the pipe be pointed towards the percipient, there is a great falling off, inasmuch as the length of the pipe approximates to the half-wave length of

\* In a still atmosphere the hot gases arising from lighted candles may be substituted for the layers of  $\text{CO}_2$ .

the sound. The experiment may be made in the lecture-room with the sensitive flame and one of the highest pipes of an organ, but it succeeds better and is more striking when carried out in the open air with a pipe of lower pitch, simply listened to with the unaided ear of the observer. Within doors reflections complicate all experiments of this kind. [R.]

Friday, January 31, 1902.

THE RIGHT HON. LORD KELVIN, G.C.V.O. D.C.L. LL.D. F.R.S.,  
Vice-President, in the Chair.

PROFESSOR A. CRUM BROWN, M.D. D.Sc. LL.D. F.R.S.

*The Ions of Electrolysis.*

THE subject of Electrolysis must always have a special interest for the Royal Institution. It was here that Davy showed its practical value by his brilliant discovery of the metals of the alkalis and alkaline earths; and it was here that Faraday laid the foundation of the scientific discussion of electrolysis; it was here that with his singular experimental skill and clearness of insight he discovered and expounded the laws of electrolysis which will always be known by his name. It is therefore with a good deal of diffidence that I stand here to continue the story. And there is much to be said: for, like all good work, Faraday's work has been fruitful, and in consequence of it, as well as of the genius and skill of subsequent investigators, we now know much about electrolysis which Faraday did not and could not know.

The great difficulty left was that of the mechanism of electrolysis. That the cation and the positive electricity travel together towards the cathode, and that the negative electricity similarly travels with the anion towards the anode, and that on their arrival at the electrodes the electricity is delivered to the metallic conductor and the matter is set free to appear as the ion itself, or to break up, or to act on the electrode, or on the solvent, or on something present in the solution; that the quantity of each ion so set free is proportional to the quantity of electricity transferred from the one electrode to the other and to the equivalent of the ion—that is, as we would put it now (if purists will allow us to speak of the atomic weight of  $\text{NH}_4$  or of  $\text{NO}_3$ ), to the atomic weight of the ion divided by its valency; all that was made out by Faraday. He had made some way in finding out how the liberated ions act, when they do act, on the things in the presence of which they find themselves; and where he led, others have followed, so that we have now many electrolytic methods of oxidation, of reduction and of synthesis, and great manufacturing industries depending on electrolysis. On this large field I do not now purpose to enter. What I wish to call your attention to this evening is the

mechanism of electrolysis, or perhaps I should say the progress that has been made towards an explanation of the phenomena.

The earlier theories, from Grotthuss\* in 1806, all assume that the decomposition is caused by the attraction of the electrodes or by the passage of the current, and that a definite electromotive force, different for each electrolyte, is required in order that decomposition shall take place. According to these theories, if the electromotive force is below that definite minimum no decomposition can occur and no current can pass.

And indeed at one time it was supposed that this was so. But Faraday, in a series of ingeniously devised and carefully executed experiments, showed that with electromotive force below the minimum necessary for the production of bubbles of gas on the electrodes, a perceptible current could pass for many days. He supposed that this small current was due to non-electrolytic conduction by the electrolyte. But the study of the phenomena of the polarisation of the electrodes led ultimately to the complete explanation by Helmholtz† in 1873 of this apparently metallic conduction by the electrolyte, and to a proof that any electromotive force, however small, sends a current through an electrolyte and gives rise to separation of the ions proportional to the amount of electricity transmitted.

The phenomena of the polarisation of the electrodes may be described shortly as follows. In the electrolysis of water (or rather of dilute sulphuric acid) it had been observed so long ago as 1802 that platinum or silver plates which had been used as electrodes acquired peculiar properties, so that for a short time the plate that had been the anode acted like the silver, and the plate that had been the cathode like the zinc of a voltaic cell, producing a short-lived and rapidly diminishing current. This observation was first made by Gautherot‡ a teacher of music in Paris, who notes the effect of the current on the tongue and states that he had succeeded in decomposing water by means of his apparatus. Shortly after, J. W. Ritter, apparently without knowing anything of Gautherot's work, made a great many observations on the same subject. I cannot refrain from reading to you a passage from a letter from Christoph Bernoulli to van Mons. I take it from the translation published in *Nicholson's Journal*, October 1805. "As Mr. Ritter at present resides in a village near Jena, I have not been able to see his experiments with his grand battery of two thousand pieces, or with his battery of fifty pieces, each thirty-six inches square, the action of which continues very perceptible for a fortnight. Neither have I seen his experiments with the new battery of his invention, consisting of a single metal, and which he calls *the charging pile*.

\* Grotthuss, *Annales de Chimie*, lviii. p. 54 (1806).

† Helmholtz, *Pogg.* 150, p. 483 (1873); Faraday Lecture, *Chem. Soc. Trans.* 39, p. 287 (1881); *Wied.* 34, p. 737 (1888).

‡ Gautherot, *Annales de Chimie*, xxxix. p. 203 (1801).

"I have frequently, however, seen him galvanise louis-d'or lent him by persons present. To effect this, he places the louis between two pieces of pasteboard thoroughly wetted, and keeps it six or eight minutes in the chain of circulation connected with the pile. Thus the louis becomes charged, without being immediately in contact with the conducting wires. If this louis be applied afterwards to the crural nerves of a frog recently prepared, the usual contractions will be excited. I had put a louis thus galvanised into my pocket, and Mr. Ritter said to me a few minutes after, that I might find out this louis from among the rest, by trying them in succession upon the frog. Accordingly I made the trial, and in reality distinguished among several others a single one, in which the exciting quality was very evident. This charge is retained in proportion to the time that the piece has remained in the circuit of the pile. It is with metallic discs charged in this manner, and placed upon one another with pieces of wet pasteboard alternately interposed, that Mr. Ritter constructs his charging pile, which ought in remembrance of its inventor to be called the *Ritterian pile*. Mr. Ritter made me observe, that the piece of gold galvanised by communication exerts at once the action of two metals, or of one constituent of the pile; and that the half which was next the negative pole while in the circle became positive, and the half toward the positive pole became negative."

Brugnatelli \* suggested that the polarisation of the plate which during the electrolysis had given off hydrogen was due to a compound of hydrogen with the metal of the electrode. But it was not until Schönbein discussed the question in 1839 † that a systematic attempt was made to settle it by experiment. Schönbein's results were in favour of the view that the polarisation is due to the formation, on the surfaces of the electrodes, of thin sheets of the products of the electrolysis.

Now the old theories assume that if we begin with very small electromotive force and gradually increase it, we have at first a state of tension, the electromotive force so to speak pulling at the ions, that this tension increases as the electromotive force increases till it becomes sufficient to pull the ions apart. If this were so there should be no current and no electrolysis till the electromotive force reaches a certain amount, and then suddenly a very great current, and something like an explosive discharge of gas; for many molecules would be in the very same state of tension and all would give way at once.

When the electrolytic decomposition of water was first observed, as it was (by Nicholson and Carlisle) immediately after the publication of Volta's first description of the pile, the great difficulty felt by every one was that the hydrogen and the oxygen came off at different places which might be far apart. Grotthuss's theory no doubt

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\* Brugnatelli, Gilbert's *Annalen*, xxiii. p. 202 (1806).

† Schönbein, *Fogg.* xlv. p. 109; xlvii. p. 101 (1839).

explained this, but after the proof of a cause of polarisation given by Schönbein, and the accumulating evidence that Ohm's law applies to electrolytic as well as to metallic conduction, no one could hold or defend Grotthuss's theory, although it was retained as a sort of makeshift until someone could think of something better. The something better was produced by Clausius in 1857.\* Clausius was one of the eminent physicists to whom we owe the kinetic theory of gases, and his theory of electrolysis is derived from an application to solutions of the ideas involved in this kinetic theory. He supposes that the molecules of the electrolyte move through the solution as the molecules of a gas move, that they collide with one another as the gas molecules do, and that it must happen that here and there ions get separated, and remain separated for a time, cation again uniting with anion when two of them meet under favourable conditions. There will thus always be some detached ions moving about just as molecules do. They will not always be the same ions that are thus detached, and a very small proportion of such loose ions will suffice to explain the phenomena. These loose ions retain in their separate condition the charges of electricity which they had when united, the cations being positively and the anions negatively charged. This is assumed to be the state of matters in any solution of an electrolyte. If now into such a solution we place two electrodes with any, however small, difference of potential, the cathode, being negative, will exercise an attraction upon the positively charged cations, and the positive anode will exercise a similar attraction on the negatively charged anions, and thus the loose ions, which before the introduction of the electrodes moved about in the liquid with no definite preferred direction, will on the whole, now that the electrodes have been introduced, move preferably, the cations towards the cathode, and the anions towards the anode, and those which are near the electrodes will be drawn to them and discharge their electric charge. This theory seems therefore to explain the phenomena. The essential difference between it and all previous theories is that Clausius does not attribute the decomposition to the current or to the attraction of the electrodes; what the attraction of the electrodes does is to separate the ions already disengaged from one another, and this the smallest electromotive force can do. The theory is so far adequate, but is it admissible? Can we suppose that hydrogen and chlorine atoms can move uncombined through the solution? It is to be noted that while Clausius does not give any opinion as to the proportion of loose ions to the total ions in any case, he assumes that this proportion increases as the temperature rises, on account of the greater briskness of the movements of the particles, and points out that this is in accordance with the fact that electrolytes conduct better as the temperature is higher. But he says, "to explain the conduction of the electricity it is sufficient that in the encounters of

\* Clausius, Pogg. ci. p. 338 (1857).



the molecules an exchange of ions should take place here and there, and perhaps comparatively rarely."

In this connection we may look at the views expressed by Williamson in his paper on the theory of etherification.\* He says, "we are thus forced to admit that in an aggregate of molecules of any compound there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition  $\text{ClH}$ , the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with other atoms of hydrogen, or what is the same thing, changing chlorine." Williamson founded this opinion on the observed facts of double decomposition. He made no application of this view to the case of electrolysis, and indeed does not explicitly mention the temporary detachment of the atoms during the process of exchange; this is wholly due to Clausius, who arrived at his views as to the exchanges going on in a solution in a way quite different from that followed by Williamson, and quite independently. It was not then known how closely double decomposition and electrolysis are connected. We may perhaps get a clearer idea of Clausius's theory by imagining the phenomenon to take place on a scale such that we could see the individual ions. Let us then imagine a large field with a large number of men in it, each mounted on a horse. We shall further suppose that all the men are exactly alike and that all the horses are exactly alike. They are moving at random, most of them at about the same rate but a few of them faster, a very few of them considerably faster, a few of them slower, a very few of them considerably slower, than the average. They move in straight lines until they meet an obstacle which makes them deviate. This obstacle will often be another man and horse. The collision will give both a shake, and will sometimes dismount one or both of the riders. When this happens each will look for a horse, and as all the horses are exactly alike the horse such a dismounted man finds and mounts will not always be the one he came down from. But in any case there will be always in the field some men without horses and some horses without men. And the quicker the average pace the larger will be the proportion of dismounted men and riderless horses to the total number of men and horses. And this not only because there will be more and, as a rule, more violent collisions, but also because the dismounted men will have more difficulty in catching horses, although to keep up the analogy of the ions we must suppose the horses to be as anxious to be caught as the men are to catch them. If it does not make my allegory too grotesque we might suppose places with attractions for men and for horses respectively, to correspond

\* Williamson, Chem. Soc. Journ. iv. p. 111 (1852).

to the electrodes, so that a man looking for a horse would on the whole rather go in the direction of lunch than away from it, and if he got near the refreshment room before he found a horse, he would look in there. An objection was made to Clausius's theory that the same thing which he supposed to happen in solution, say of hydrochloric acid, ought also to happen in the gas. We are not yet in a position to discuss this point with much prospect of obtaining a perfectly satisfactory explanation of the difficulty, although some progress towards an intelligible theory has been made, but at the risk of being tedious, I may indicate that my allegory may show us that we need not despair of finding in due time an answer. Let us suppose that in the field there are not only men and horses but also a large number of other moving objects, let us say, by way of example, cows. It seems plain that whether the presence of the cows would increase the chance of a man being dismounted or not, it would sensibly interfere with his chance of catching a horse if he were. And it will be admitted that the nature and size of these other moving objects must exercise an influence on the proportion of horseless men and riderless horses to the total number. But these other moving objects represent the molecules of the solvent, so that we need not be surprised when we find that the electrolytic conductivity is affected by the nature of the solvent, and that where there is no solvent the conductivity is very small or even nothing.

A very important question was left only partially answered by Faraday. It is, What substances are electrolytes? Faraday considered the water in dilute acid as the electrolyte, and the acid as a substance having the power of increasing the conductivity of the water. When a solution of sulphate of copper was electrolysed, he supposed that the water was primarily decomposed and that the metallic copper was a secondary product reduced by the nascent hydrogen. He says,\* "I have experimented on many bodies, with a view to determine whether the results were primary or secondary. I have been surprised to find how many of them, in ordinary cases, are of the latter class, and how frequently water is the only body electrolysed in instances where other substances have been supposed to give way." From our present point of view many of us would rather say that the direct electrolysis of water very rarely occurs, except to a very small extent.

In 1839 Daniell began a series of ingeniously devised and skilfully executed experiments with the view of determining, in the case of salt solutions, whether it is the salt or the water which is primarily electrolysed. The results appeared in two letters from Daniell to Faraday in 1839† and 1840,‡ and in a paper by Daniell and W. A. Miller in 1844,§ all published in the Transactions of the Royal

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\* Faraday, *Experimental Researches in Electricity*, par. 751 (1834).

† Daniell, *Phil. Trans.* 1839, p. 97.

‡ *Op. cit.* 1840, p. 209.

§ Daniell and Miller, *Phil. Trans.* 1844, p. 1.

Society. The purpose of these investigations was attained, and it was completely proved that in reference to their behaviour as electrolytes there was no difference between say potassium chloride and potassium nitrate, except that in the latter some ammonia was formed at the cathode by the reducing action of the nascent hydrogen, and it was clearly shown that from an electrolytic point of view all the oxygen acids and their salts fell into line with hydrochloric acid and the chlorides, and that  $\text{NH}_4$  was electrolytically perfectly analogous to K. There is, however, an interest in these papers beyond this important result. In the earlier part of the work the authors measured the amount of electrolysis not only by "the amount of ions disengaged at either or both electrodes by the primary action of the current or the secondary action of the elements," but also tried to obtain a check to this way of measuring, by using a diaphragm in the electrolytic cell, and analysing the contents of the two parts of the cell, the one on the anode side and other on the cathode side of the diaphragm. This check was "founded on the hypothesis that the voltaic decomposition of an electrolyte is not only effected by the disengagement of its anion and cation at their respective electrodes, but by the equivalent transfer of each to the electrodes, so that the measure of the quantity of matter translated to either side of the diaphragm might be taken as the measure of the electrolysis." They soon found that this hypothesis was unfit to give any such measurement, and in the paper of 1844 state that their results show that the hypothesis of equivalent transfer of the ions, "although generally received, is itself destitute of foundation."

The non-equivalent transfer of the ions, incidentally observed by Daniell and Miller, and imperfectly measured by them in a few cases, was made the subject of a long and elaborate series of experiments by Hittorf. The work extended over six years from 1853 to 1859\* and is a monument of patient labour and of happy adaptation of means to a clearly perceived end. The importance of the work was not at first recognised by either physicists or chemists, indeed its meaning was scarcely understood. I shall try to put before you as shortly as I can an outline of the ideas involved in the work, and of the most important conclusions arrived at by Hittorf. As the anions and the cations are separated at their respective electrodes in equivalent quantity, that is, in the case where the valency of anion and cation is the same, in equal numbers, it never occurred to any one to doubt that they travelled towards the electrodes at the same rate, until Daniell and Miller showed that this hypothesis is erroneous. To follow their reasoning and that of Hittorf we may take an imaginary case, and suppose an electrolyte  $\text{MX}$  with its cation  $\text{M}$  and its anion  $\text{X}$  of such character that these ions when separated at the electrodes can be removed from the solution completely and at

\* Hittorf, Pogg. lxxxix. p. 177 (1853); xcvi. p. 1 (1856); ciii. p. 1 (1858); cvi. pp. 337 and 513 (1859). Arch. Néerland. (II.) vi. p. 671 (1901).

once, and that the electrolysis is carried on in a vessel provided with two compartments, one containing the cathode and the other the anode, such that whatever happens at an electrode shall affect only the contents of the compartment containing that electrode, and so arranged that the liquid contained in each compartment can be completely removed from it and analysed. Now, let us first suppose  $MX$  to be such that its ions travel at the same rate. In the time then in which one  $M$  has entered the cathode compartment one  $X$  has left it. There is at this moment an excess of two  $M$ 's in this compartment, these are deposited at the cathode, and now the concentration of the solution in this compartment is diminished by one  $MX$ . Similarly at the anode during the same time one  $X$  has entered and one  $M$  has left, two  $X$ 's have been deposited and the solution has lost one  $MX$ . In this case, then, where the two sets of ions travel at the same rate, the loss of solute is the same at the two electrodes. Let us now suppose an extreme case in which one of the sets of ions (say the cations) does not travel at all. In the time in which one  $X$  leaves the cathode compartment no  $M$  enters it, the excess of one  $M$  is deposited, and the solution here has lost one  $MX$ . At the anode one  $X$  has entered and no  $M$  has left, the  $X$  is deposited, and the solution here has lost no  $MX$ . Again, take the case that the anions travel twice as fast as the cations. Here in the time in which one  $M$  enters the cathode compartment two  $X$ 's leave it, the excess of three  $M$ 's is deposited, and the solution has lost two  $MX$ 's. At the anode during the same time one  $M$  has left and two  $X$ 's have entered, the three  $X$ 's have been deposited and the solution has lost one  $MX$ . Of course it will be seen that the excess of one kind in a compartment consists not only of what enters it, but also of the excess resulting from the departure of the other kind. Without taking any more cases we at once see that the speed of the cation is to that of the anion as the loss of solute at the anode is to that at the cathode. This non-equivalent transfer has sometimes been described in another way. It has been said that the ions go at the same rate, but that at the same time the solute as a whole is being moved towards one of the electrodes. But this really is the same thing. If we imagine two processions walking with the same length of step and the same number of steps a minute in opposite directions on such a moving platform as that in the Paris Exhibition, we might no doubt say that the two *walked* at the same rate, they could not be said to *travel* at the same rate. Hittorf's way of putting it is not only the simpler way, it is the only way that agrees with what has since been made out as to the rate of movement of the ions.

Hittorf's work had to wait long for recognition, but we now know its great importance, not only on account of the large number of accurate measurements, but also because of the general conclusions he drew from them. He deduced from the transfer numbers conclusions as to the nature of the solute, showing, for instance, that solution of stannic chloride electrolyses as hydrochloric acid, the stannic chloride

being completely hydrolysed. He also showed that such double salts as  $\text{KCN}, \text{AgCN}$ ;  $2\text{KCl}, \text{PtCl}_4$ ; and  $\text{KCl}, \text{AuCl}_3$ , have potassium for their only cation, the silver, the platinum and the gold forming part of the anion. He also showed that  $2\text{KI}, \text{CdI}_2$  behaves as a single salt with K as cation when the concentration is great, but as two salts with cadmium as well as potassium as cation in dilute solution. In these and in similar cases, Hittorf made a valuable contribution to the theory of double salts. But perhaps the most striking generalisation is that contained in the words "electrolytes are salts," and his very instructive comparison of the readiness with which a substance enters into double decomposition and the readiness with which it can be electrolysed. With the fairness to his predecessors which is characteristic of him, he quotes an almost forgotten statement of Gay-Lussac to something like the same effect.

Ladies and Gentlemen,—I wish here to tell you that within the last three weeks, Professor Hittorf entered on the fifty-first year of his professorship. The officials of the Royal Institution have authorised me to ask our Chairman, Lord Kelvin, to send your congratulations to Professor Hittorf on his jubilee.

We now come to another turning point in the development of the theory of electrolysis, inseparably associated with the name of Kohlrausch.\* It is to Kohlrausch and to those who worked with him that we owe the methods for the accurate determination of the conductivity of electrolytes. I need not give a description of the apparatus. It is now used in every laboratory, and by means of it a series of observations of the conductivity of an electrolyte can be made at different concentrations in a very short time. An early result of Kohlrausch's investigation was his discovery that "all acids which have been examined in strong solutions show, for a definite proportion of water, a maximum of conductivity," and he shows that for many other electrolytes there is a solution which conducts better than one either a little more or a little less concentrated. Thus the maxima of conductivity of the following acids are at the following percentages:  $\text{HNO}_3$  29.7 per cent.;  $\text{HCl}$  18.3 per cent.;  $\text{H}_2\text{SO}_4$  30.4 per cent.;  $\text{HC}_2\text{H}_3\text{O}_2$  16.6 per cent. "The maximal acetic acid conducts at least 38,000 times better than concentrated acetic acid." In connection with this he says, "we do not know one single liquid, which at ordinary temperature is, by itself, a good electrolytic conductor." He refers the trace of conductivity in  $\text{H}_2\text{SO}_4$  to the dissociation into water and  $\text{SO}_3$  observed by Marignac and by Pfaunder, and observes that as up to the present time we know only

\* Kohlrausch and Nippoldt, Pogg. cxviii. p. 280 (1869); Kohlrausch, Pogg. Jubelband, p. 290 (1874); Kohlrausch and Grottrian, Pogg. cliv. pp. 1 and 215 (1875); Grottrian, clvii. p. 130 (1876); Kohlrausch, clix. p. 233 (1876). Göttinger Nachrichten, 1876, p. 213. Wied. vi. p. 1 (1879); xi. p. 653 (1880).

mixtures which at ordinary temperature conduct well, the supposition is not unnatural that it is mixture that makes electrolytes good conductors. And again, if what has been said is correct, we must, in order to have good conduction, protect the wandering constituents from frequent meeting with one another, and this service is performed by the solvent, which makes it possible for the ions to get over a part of their journey—and so much larger a part the more solvent there is—without re-forming molecules. It is this suggestion which I ventured a little while ago to put into an allegorical form.

In order to compare the conductivity of one electrolyte with that of another, it is necessary that we choose comparable quantities of the two, and there is no difficulty in seeing that such comparable quantities are those decomposed by the same current of electricity—that is to say, the electro-chemical equivalents of the electrolytes. Accordingly, instead of expressing the concentration in percentage of the solute, Kohlrausch uses “molecular numbers.” The molecular number of a solution is the quantity, in grams, of the solute contained in a litre of the solution divided by the equivalent of the solute. Dividing the conductivity of a solution by its molecular number gives its molecular conductivity. It will be seen that “molecular” is not used here in its ordinary chemical sense, but as the meaning is quite distinctly stated no confusion need arise. Kohlrausch showed that the molecular conductivity increases as the solution becomes more dilute, and with extreme dilution approaches a constant value.

I now show an experiment to illustrate this.

The apparatus\* consists of an electrolytic cell in the form of a tall rectangular trough, the back and front being broad plates of glass, while the sides are composed of narrow strips of wood completely lined with silver foil. The bottom of the cell is made of non-conducting material. The two sheets of silver serve as electrodes, being connected to binding screws by means of external wires. The cell is introduced into a battery circuit along with a galvanometer of low resistance. If the cell be filled with pure water there is scarcely an appreciable current transmitted. On removing the water and pouring in 20 cc. of a 4-normal silver nitrate solution, so as to cover the bottom to a depth of a few millimetres, a current passes as indicated by the galvanometer. If pure water be now added in successive portions and the solution stirred after each addition, an increase in the strength of the current is observed, the increase being greatest after the first dilution, and becoming less with each succeeding dilution, so that a maximum is approached. In this experiment the distance between the electrodes is constant, and the area of the electrodes and of the cross-section of the conducting solution are proportional to the volume of the solution, and the quantity of the

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\* From a paper by Noyes and Blanchard, in the *Zeitschrift für physikalische Chemie*, xxxvi. p. 9 (1901).

salt is constant; therefore any change in the strength of the current means a corresponding change in the molecular conductivity of the dissolved salt. The molecular conductivity, therefore, increases with the dilution, and asymptotically approaches a maximum.

I cannot here enter into a description of the great experimental difficulties connected with the determination of the conductivity of extremely dilute solutions, but I may refer to one of them, namely the small but variable conductivity of the water used in preparing the solutions. There seems now to be no doubt that water is in itself an electrolyte. But the purest water that has been obtained has a conductivity of only about  $10^{-10}$  as compared with that of mercury as unit. The minutest traces of salts greatly increase the conductivity, so that ordinary distilled water has a conductivity of  $3 \times 10^{-10}$  or more. With solutions of moderate dilution the variation of this very small quantity is of little consequence, but with extremely dilute solutions the conductivity to be measured is of the same order as that of the water.

For our present purpose the most important conclusion drawn by Kohlrausch from his observations is his law of the independent rate of motion of the ions in dilute solutions. The rate of motion of any ion towards the electrode depends on the gradient of potential. But Kohlrausch shows that the rate of motion of each ion in dilute solution is proportional to a number, the same whatever be the other ion of the electrolyte. Thus the rate at which the cation K moves towards the cathode in dilute solution, is the same in solutions of KCl,  $\text{KNO}_3$ ,  $\text{KC}_2\text{H}_3\text{O}_2$ , etc. Kohlrausch gives these numbers for six cations and ten anions. The results calculated from these numbers agree well with the observed conductivities.

Methods have been devised for directly observing and measuring the rate at which ions travel. In this connection I may specially mention the names of Oliver Lodge, Whetham, and Masson. These measurements agree very well with the rates calculated by Kohlrausch.

I now show an experiment indicating a way in which such measurements can be made.

The apparatus \* consists of a glass U-tube, with a long stopcock-funnel connected to the lower part of it. The tube is nearly half filled with a dilute (about 0.03 per cent.) solution of potassium nitrate, and then about the same quantity of a solution of potassium permanganate, of the same conductivity as the other solution, is slowly introduced by means of the funnel. The permanganate solution is loaded with urea (a non-electrolyte) so as to make it denser than the nitrate solution; the permanganate solution now lies in the lower part of the U-tube with a sharp interface between it and the nitrate solution above it in each limb of the tube. If now we connect

\* Experiment from a paper by Nernst. in the *Zeitschrift für Elektrochemie*, iii. p. 308 (1897).

the electrodes, which were preliminarily inserted into the upper parts of the two limbs of the tube, with a battery with high difference of potential a current will pass, and a transference of ions will take place, cations (K) towards the cathode and anions ( $\text{NO}_3$  and  $\text{MnO}_4$ ) towards the anode, and the column of pink colour will rise in the limb containing the anode and fall by an equal amount in the other. By this means an approximation can be made to the rate of travel of the ions.

We now come to a new chapter beginning with 1887; but before entering on it we must turn aside for a little to a subject which does not at first sight seem to have a very close relation with the matter we have in hand. The subject is that of what may be called the osmotic phenomena. These are all connected with the concentration or with the dilution of solutions. They all involve the idea of the work done in concentrating a solution. We need not discuss the theory of these phenomena, we are interested in them now only as they give us methods of ascertaining the molecular concentration of a solution. In 1883\* Raoult showed that in the case of a great many substances, equimolecular solutions (with the same solvent) have the same freezing-point. In 1886† he showed that equimolecular solutions with the same volatile solvent have the same boiling-point. Molecular is here used in its ordinary chemical sense. These discoveries were eagerly taken up by chemists as promising an important addition to the means at their disposal for determining the molecular weights of substances. Convenient arrangements for applying the methods were devised by Beckmann,‡ and soon came into use in nearly every laboratory. They were almost exclusively used for the determination of the molecular weight of organic substances, and have been found trustworthy in such cases. When, however, van't Hoff§ in his study of the theory of solutions concluded from theoretical considerations that the depression of the freezing-point and the rise of the boiling-point are proportional to osmotic pressure in the case of dilute solutions, the observations made by Raoult and others furnished a number of facts ready for testing the theory. He found that, while in many cases the osmotic pressure calculated from his formula  $PV = RT$  agreed, within the limits of experimental error, with the value calculated from the observation, there were a very considerable number where the observed value differed from that given by the formula. He accordingly modified the formula by the introduction of a factor  $i$ , so as to make it  $PV = iRT$ . This factor  $i$

\* Raoult, *Compt. rend.* xciv. p. 1517; xcv. pp. 187 and 1030 (1882); xevi. p. 1653; xcvii. p. 941 (1883).

† Raoult, *Compt. rend.* ciii. p. 1125 (1886); civ. pp. 976 and 1430; cv. p. 857 (1887). *Zeitschrift f. physik. Chemie*, ii. p. 353 (1888).

‡ Beckmann, *Zeitschrift f. physik. Chemie*, ii. pp. 638 and 715 (1888); iv. p. 532 (1889); viii. p. 223 (1891).

§ Van't Hoff, *Zeitschrift f. physik. Chemie*, i. pp. 500-508 (1887).



is unity in the cases where observation by Raoult's method gives results agreeing with the formula  $PV = RT$ , in other cases it is greater or less than unity, and indicates the extent of the disagreement. Arrhenius, to whom Van't Hoff showed these numbers, pointed out that all the substances which had  $i$  greater than unity were electrolytes, and that the deviation had to do with their splitting up into ions. Arrhenius\* had before this time (1887) been working at the subject of electrolysis and of the relation between the readiness with which substances undergo electrolysis and the readiness with which they enter into chemical reactions. He had been looking for an explanation of the fact that the conductivity of a solution of an electrolyte is not proportional to its concentration, and had come to the conclusion that this must depend on some of the molecules of the solute being "active," that is, taking part in the conduction, while others were inactive, behaving like molecules of a non-electrolyte, and that the proportion of active molecules increases with dilution.

Van't Hoff's factor  $i$  enabled Arrhenius to give precision to these ideas, and in 1887† he formulated the theory that the "active" molecules were those which were split into ions. It was now possible to calculate  $i$  in two ways and compare the results. Arrhenius gives a list of eighty-four substances, for which there existed at that time data for such calculations, and calculating the value of  $i$  as deduced on his new theory from the conductivity, compares it with the value of  $i$  derived from freezing-point observations in each of the eighty-four substances. The agreement does not at first sight strike one as very close, but there are several circumstances which have to be considered in judging them. The whole mass of published observations was taken, the limits of probable error are very different in different cases, and the freezing-point measurements were all made at temperatures a little below  $0^{\circ}$ , while the conductivity measurements were made at  $18^{\circ}$ . The comparison was made, not as a demonstration of the theory, but rather as a preliminary trial with such materials as were at hand. The real testing of the theory necessarily came later. So I think we may agree with Arrhenius that, considering all the circumstances, the agreement is not unsatisfactory, except in the case of nine of the substances, and that most of these nine cases are liable to suspicion on other grounds. In 1887, almost at the time when Arrhenius published the paper of which I have just been speaking, Planck‡ discussed the subjects of the diminution of the vapour pressure and the lowering of the freezing-point in dilute salt solutions from the thermo-dynamic point of view, and starting from the principle of the increase of entropy, deduced formulæ connecting these quantities with the molecular

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\* Arrhenius, Bihang till kongl. Svenska vetensk. Akad. Handlingar, 1884 Nos. 13 and 14.

† Arrhenius, Zeitschrift f. physik. Chemie, i. p. 631 (1887).

‡ Planck, Wied. xxxii. p. 495 (1887).

weight. He says, in conclusion, "This formula claims exact numerical validity. It gives for most substances a greater molecular number than that usually assumed, i.e. a partial or complete chemical decomposition of the substance in the solution. Even if the consequences of this proposition should require an essential modification of the generally prevailing views as to the constitution of solutions, I do not know any fact which shows it to be untenable. Indeed, many observations in other departments (the proportionally strong affinities of dilute solutions, which remind one of the properties of the nascent state, the easy decomposability by the weakest galvanic current, the phenomena of internal friction), are directly in favour of the view that in all dilute solutions a more or less complete decomposition of the molecules of the dissolved substance takes place. Besides, this conception adapts itself well to the opinions developed by L. Meyer, W. Ostwald and S. Arrhenius on the state of the molecules of dissolved substances, as it only goes a step further and fixes numerically the degree of the decomposition."

An objection was taken to Planck's argument. It was said that as his formula contains the ratio of the molecular numbers of the solute and of the solvent, it could not be inferred that that of the solute is greater than its formula leads to, for it might be that the molecular number of the solvent is less than that indicated by its formula. Planck's answer was immediate and obvious. In any expression in which the molecular number of the solvent appears, there also appears as a factor the molecular weight. For instance, in the formula for the depression of the freezing-point the molecular number of the solvent is multiplied by the latent heat of one molecule of the solvent, and similarly in other cases. So that it makes no difference what molecular weight we assume for the solvent, and the use of its molecular number is merely a convenient way of expressing its quantity.

This increase in the number of the molecules, or splitting into ions, was called "electrolytic dissociation." It will be seen that it is what Lodge in 1885, in speaking of Clausius's theory, called dissociation. But while it has some obvious resemblances to the dissociation of a gas, there are very striking differences between the cases, and perhaps some of the difficulties in the way of the acceptance of the theory may have arisen from the use of the same word for two things differing so much. We need not, however, discuss the name, but it is well to look for a little at the essentially different nature of the things. This essential distinction consists in the products of the electrolytical dissociation being charged, the one set with positive, the other set with negative, electricity, so that, while in the body of the solution they can move about independently, they cannot be separated by diffusion as the products of the dissociation of a gas can. It is true that the quicker moving ions can, to a small extent, forerun the slower moving ions, and diffuse a little further into pure water or into a more dilute solution, as is shown by the fact that when two solu-

tions of the same electrolyte of different concentration are in contact there is a difference of electric potential between them, but they cannot be separated to any weighable extent in this way. In order to separate from one another two gases uniformly mixed, a certain calculable amount of work has to be done, so that after a gas has been dissociated and wholly or partially converted into a mixture of the two gaseous products, some work has still to be done to get them separately. So it is also in the case of electrolytic dissociation; but while in the former case the decomposition work is the main thing, and the separation work very small, in the latter it is quite the other way. Here the heat of dissociation, that is the work spent in decomposing the electrolyte into its ions, is small (indeed sometimes negative), while the work to be done to *separate* the ions is always very much greater. Indeed we may quite correctly say that in most highly dissociated solution of hydrochloric acid the hydrogen and the chlorine are still very firmly united, not indeed atom to atom, but each atom of the one kind to all the atoms of the other kind within a certain distance from it. A man does not lose his money when he takes it out of his pocket and puts it into a bank. He does indeed lose his relation to the individual gold and silver coins, and does not know and does not care where these particular pieces of metal are, but he is interested in knowing that they or their like are at his command, and the same sort of work will be required to impoverish him whether his money is in the bank or in his pocket. (I assume, of course, that the bank of our present imagination cannot become insolvent.)

I have said that the test of the theory would come later. It has been going on since 1887, and if time would allow I could give you many cases in which deductions from the theory have been found to agree with close quantitative accuracy with experimental observations. I shall mention only the first, still among the most important, namely Ostwald's determination of the affinity constants, and his application of Guldberg and Waage's principle to the ions. I could also give you instances in which there have been discrepancies, or apparent discrepancies, and show how in some of these cases the difficulties have been cleared up. The history of this theory has in fact so far been that of every useful theory, for it is in this way only that a theory does its work. I shall select two points for illustration, not because they are more important than others, but because I can illustrate them by means of experiments which do not occupy much time, and can be made visible in a large room. The first has reference to the question, What are the ions in the case of a dibasic acid? As  $\text{HNO}_3$  gives as its ions  $\text{H}$  and  $\text{NO}_3$ , so we might expect  $\text{H}_2\text{SO}_4$  to give  $2\text{H}$  and  $\text{SO}_4$ . But we find that until the dilution has advanced to a considerable extent the ions of sulphuric acid are mainly  $\text{H}$  and  $\text{HSO}_4$ . This is quite in harmony with the chemical action of  $\text{H}_2\text{SO}_4$ , for, as every chemist knows, at moderate temperatures we have the action  $\text{H}_2\text{SO}_4 + \text{NaCl} = \text{HCl} + \text{NaHSO}_4$  and the temperature has to be raised in order to get the action  $\text{NaHSO}_4 + \text{NaCl}$

=  $\text{HCl} + \text{Na}_2\text{SO}_4$ . In the first of these experiments we take as the electrolyte a concentrated solution of potassium hydrogen sulphate  $\text{KHSO}_4$ . This gives the ions  $\text{K}$  and  $\text{HSO}_4$ . The latter go to the anode and there, on being discharged, form persulphuric acid, or its ions, and potassium persulphate  $\text{K}_2\text{S}_2\text{O}_8$ , being sparingly soluble, crystallises out. This is the method by means of which Dr. Marshall discovered the persulphates. The next experiment will illustrate the formation and discharge at the anode of the anion  $\text{SO}_4$ . We have here dilute sulphuric acid with which is mixed a little manganous sulphate  $\text{MnSO}_4$ . The ion  $\text{SO}_4$  when discharged, adds itself to  $2\text{MnSO}_4$  and forms manganic sulphate  $\text{Mn}_2(\text{SO}_4)_3$ , recognised by its red colour. This, even in acid solution, is quickly hydrolysed, giving insoluble manganic hydrate.

The other point I wish to illustrate is the application of Guldberg and Waage's principle to ions. Without entering into any general discussion of this question, I shall merely say that theory leads to the result that the addition of a soluble acetate to a solution of acetic acid diminishes the concentration of  $\text{H}$  ions, and so makes the solution less effectively acid. This was experimentally proved by Arrhenius in 1890,\* by measuring the rate at which cane-sugar is inverted by acetic acid alone, and with varying quantities of sodium acetate added to it. But as such an experiment cannot be made visible to a large number of spectators at once, I thought of a way of showing the same thing, which, while not capable of the same degree of accuracy, would prove the principle qualitatively. I have here a solution of ferrous acetate to which I have added enough acetic acid to prevent the precipitation of ferrous sulphide on the addition of sulphuretted hydrogen. I add sulphuretted hydrogen, of course no precipitate is formed. I now add a solution of sodium acetate mixed with rather more than three equivalents of acetic acid, so as to make it plain that the effect is not due to the formation of an acid acetate, and you see that we have at once a precipitate of ferrous sulphide. To show that the addition of the water has not produced the result, I add to another portion of the same solution as much water, and you see that no precipitation takes place.

I have not spoken of non-aqueous solutions. At the rise of the dissociation theory, these were generally supposed to be non-conductors, but many of them have now been examined both by scientific workers in the old world, and very specially by our colleagues on the other side of the Atlantic, and been found to conduct electrolytically. It seems likely that these investigations will throw much light on the influence of the solvent on the conductivity of the dissolved salt. Particularly interesting is the relation, indicated in some cases, between the specific inductive capacity of a solvent and the dissociation of the dissolved salt. But this is one of the questions not yet ripe for treatment in a discourse such as this.

\* Arrhenius, *Zeitschrift f. physik. Chemie*, v. p. 1 (1890).

I had also thought of saying something as to the atomic character of electricity, and the compounds of electricity with what we may venture to call the other chemical elements, and had even some idea of poaching on Lord Kelvin's domain of "Aepinus atomised," but time has saved me from this.

I have been describing the history of the theory of electrolysis from the time of Faraday, in such a way as is possible within the limits of an hour. I have necessarily omitted mention of many active, able and successful workers, and I cannot in every case justify the omission except by referring to the time limit. I have as far as I could explained the evidence which we have for the theories described, but I have not intended to argue for or against the essential truth of them. I have sometimes been asked in reference to the theory of electrolytic dissociation, Do you really believe it to be true? My answer to that question is, I believe it to be an eminently useful theory. It has led to a great deal of most valuable experimental work. It has enabled us to group together things that without its help seemed very little connected. It has led to the discussion of problems that could scarcely, without its suggestion, have occurred to any one. It does not seem to be exhausted, and I look forward to much good to be got from it yet, and therefore I am willing to take it as a guide. But I do not look on it as an infallible guide; we cannot expect, we do not need, an infallible guide in physical science. A long life may be anticipated for this theory; if that be so, we may be sure that it will undergo modifications, for if it is to act, it will be acted on.

Nothing but good can come from the fullest discussion, either of the theoretical basis or of the experimental evidence for or against a theory. No great principle in science or in law can be satisfactorily settled without full argument by competent advocates on both sides, and the eager hunt for evidence by those who attack and by those who defend, will lead to a more complete investigation of the whole field than would be attained without such—shall we call it partisan—interest.

[A. C. B.]

Friday, February 21, 1902.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.L. F.R.S.,  
President, in the Chair.

W. DUDELL, Esq.

*Musical and Talking Electric Arcs.*

It is almost exactly a century since the discovery, and first exhibition of the electric arc in the lecture theatre of the Royal Institution by Sir Humphry Davy. During these hundred years attention has been chiefly centred on the light given out by the arc and on its practical utilisation. This evening, however, I will treat more particularly of the sounds it can produce. It is only of late years that any interest has been taken in these sounds, and this interest has chiefly originated from the work of Mrs. Ayrton, who classified and described the noises which arcs produce under different conditions of working.

The sounds emitted by electric arcs can be divided into two classes—those produced spontaneously, and those due to outside causes acting on the arc itself or on the circuit supplying it. In either case the sound waves seem due to the rapid variations in the volume of the vapour column which exists between the two electrodes. If the current through any direct current arc be increased or decreased slowly, and if the vapour column, or better still, its image projected on a screen be examined, it will be at once apparent that an increase in the current flowing through the arc is accompanied by an increase in the size of the vapour column, and vice versa. Let the current be periodically increased and decreased, and the vapour column will also expand and contract periodically, and if the variations in the current and the consequent periodic expansion and contraction of the vapour occurs with sufficient frequency, audible sounds are produced. This can easily be demonstrated either by causing part of the direct current which flows through the arc to pass through and operate an electrically driven tuning-fork, or by adding to the direct current flowing through the arc an alternating current.

The sensibility of the arc to small variations in the current supplying it is really surprising; for instance, the small fluctuations in the current supplied by a direct current dynamo, caused by the commutator segments passing under the brushes, can generally be distinctly heard in any arcs supplied by it. A Wehnelt or other powerful interruptor connected to the street mains will cause any

arcs fed from these mains to give out the characteristic noises, even though considerable distances intervene between the points of connection to the mains.

In some experiments on the resistance of the arc, in the course of which a small alternating current of high frequency was added to a steady direct current, I found that if even as small an alternating current as  $\frac{1}{1000}$  ampere was passed through an arc taking 10 amperes direct current, a distinctly audible note was produced by the arc at frequencies ranging from a few hundreds up to 8000 periods per second; and further experiments showed that if the added alternating current was only  $\frac{1}{20}$  to  $\frac{1}{10}$  ampere, the note did not become inaudible until frequencies as high as 30,000 periods per second were reached.\*

This great sensibility of the arc to small and rapid changes in the current through it at once suggests that the arc might be used as a telephone receiver. This was first tried experimentally by Herr Simon,† who caused the current from an ordinary microphone to flow round one coil of a mutual induction, or transformer, the second coil of which was placed in series with an arc. The variations in current flowing through the microphone due to speaking into it, induce corresponding currents in this latter coil and through the arc, causing the arc to give out sounds similar to those made near the microphone. By this means the arc may be caused to sing, whistle, or even talk distinctly.

There are a large number of other ways of superposing the microphone current or the direct current through the arc, the microphone may be shunted by an inductive or non-inductive resistance and placed directly in series with the arc; or the microphone may be connected in series with a battery and highly inductive coil, the terminals of the latter coil being connected direct to the arc terminals through a condenser, or the microphone and battery may be connected to the primary of a transformer the secondary of which is connected in series with a condenser as a shunt to the arc. I have usually found the last-mentioned arrangement give the best results.‡

Any good microphone will work, though the resulting speech from the arc varies greatly according to the microphone and the battery power used. A "Hunningscone" or "Delville" with two accumulators will, if carefully adjusted, give loud and distinct speech.

As the sound-waves are produced by the variations in the volume of the vapour column, it is natural that the loudness will depend on its size. In order to obtain loudness it is therefore necessary to use a long flaming arc and a fairly large current; such arcs can be best produced by using cored carbons or by introducing impurities, such

\* Journal of the Institution of Electrical Engineers, 1901, vol. 30, p. 238.

† Annalen der Physik und der Chemie, 1898, vol. 64, p. 233.

‡ Journal of the Institution of Electrical Engineers, 1901, vol. 30, p. 239; Elektrotechnische Zeitschrift, 1901, pp. 197 and 510.

as the salts of the metals of the alkaline earths, into the arc. An easy way to do this is to use a glass rod as a core to one of the electrodes, the sodium from the glass making it easy to burn an arc an inch or two long.

Not only is the vapour column of the arc so sensitive to any changes that may take place in the current that it can follow and reproduce all the numerous vibrations which constitute articulate speech, but I have also found that the intensity of the light given out by the arc is also capable of following very rapid small changes in the current. Thus, if the direct current through the arc be increased and decreased rapidly even over a small range, the light emitted will increase and decrease in a similar manner.\*

The light given out by one of the talking arcs varies in intensity in a manner corresponding to the vibrations which form the words the arc is saying, although the eye does not appreciate the fact, so that if the light were allowed to fall on any apparatus or substance which was sensitive to such rapid changes in the intensity of its illumination and which could reproduce such variation of its illumination as corresponding mechanical movements, then it would be possible to reconvert the variation of the light into sound waves again. One such substance is the metal selenium, which, when suitably prepared, has the property that its electrical resistance depends on whether the light falling on it is strong or weak; in a strong light its resistance is much lower than in a weak light.

An arrangement of selenium and electrodes to show the effect of light on the resistance of selenium is generally called a selenium cell.

On this basis Herr Simon† has founded a method of light telephony: in his method the light given out by a talking arc at the transmitting station is collected by a lens or reflector and focussed either directly or by means of other lens and reflectors on a selenium cell placed at the distant receiving station. This selenium cell is connected in series with a battery and a telephone receiver in which the transmitted speech is received. The action of the arrangement is as follows; talking to the microphone at the transmitting station causes the currents through it to vary, increasing and decreasing the current in the talking arc; each increase of the arc current is accompanied by an increase in the light given out, which, by means of the reflectors and lens, increases the illumination of the selenium cell at the distant receiving station. The increase of illumination causes the cell's resistance to fall and allows the battery to send a larger current through it and the telephone receiver, so that every increase of current through the talking arc produces a corresponding increase in the current through the telephone receiver. Thus the variations of current due to the microphone are transmitted along the beam of

\* Journal of the Institution of Electrical Engineers, 1901, vol. 30, p. 236.

† Elektrotechnische Zeitschrift, 1901, pp. 197 and 513.



light as variations in its intensity, and are faithfully reproduced in the telephone receiver, conveying sounds and speech just as if connecting wires had been established between the two stations.

Transmission of speech by this method has, I believe, been already accomplished over distances of several kilometers by Herr Ruhmer.

A further development of the uses of the talking arc, originated by Herr Ruhmer,\* is the production of a new phonograph founded on similar principles. A permanent record of the variations of the light emitted is obtained by photographing on a long rapidly moving film the light given out by a talking arc so as to obtain, after development, a band of deposit, the changes of density along the length of which are a record of the variations in the intensity of the light emitted by the talking arc. If such a film be subsequently caused to travel at the same speed as during the recording, and if a beam of light be passed through it on to a selenium cell, the intensity of the light beam and the illumination of the cell will vary, and speech will be reproduced in a telephone receiver connected in series with the cell as before. This new phonograph adds one more to the methods, mechanical, magnetic, and chemical, by which sound waves can be permanently recorded, and it should give us much information as to the nature of sounds owing to the ease with which the record can be visually examined.

The second part of my subject treats of quite a different property of the electric arc, a property by means of which a direct current can be automatically converted into an alternating current of almost any frequency. This property is the instability of the arc under certain conditions.

Before proceeding further I will recall the properties of the discharge (or charge) of a condenser, or Leyden jar, through an inductive circuit. Lord Kelvin proved that if the resistance of the inductive circuit be below a certain critical value (depending on the capacity of the jar and self-induction of the circuit) then the discharge current would not flow continuously round the circuit in one direction till the jar was discharged, but would first flow round the circuit in one direction and then in the other, executing a series of swings or oscillations like a pendulum, the maximum value of the current growing less and less each swing, until the oscillations finally died away and the jar was discharged. If the resistance of the circuit was so small that it could be neglected, Lord Kelvin also showed that the periodic time, or time taken for the current to rise from zero to a maximum in one direction, then die away, reach a maximum in the opposite direction and again come to zero, was given by the expression

$$\text{Periodic time} = 2\pi\sqrt{L.F.}$$

where  $F$  is the capacity of the condenser or Leyden jar and  $L$  is the self-induction of the circuit. So that the frequency of the oscillations, or the number of complete swings which can take place in one second, is the reciprocal of the above or

$$\text{Frequency} = \frac{1}{2\pi\sqrt{LF}}.$$

Such a circuit in which the discharge of the condenser is oscillatory I will refer to, in what follows, as an oscillatory circuit, and the above periodic time as the periodic time of the circuit.

If an unstable arc is made to form part of an oscillatory circuit then any oscillations in this circuit, instead of dying away as they would do were the arc not present, will persist indefinitely forming an alternating current, the energy required being automatically converted by the unstable arc into a suitable form to maintain them.

The electrical instability that is necessary for this purpose, is that if the current  $A$  through the arc be increased by any small quantity  $\delta A$  then the potential difference  $V$  between its terminals must decrease by an amount  $\delta V$  so that the ratio  $\frac{\delta V}{\delta A}$  will be a negative quantity. Messrs. Frith and Rodgers \* determined the value of the ratio  $\frac{\delta V}{\delta A}$  for a large number of arcs between carbon electrodes, and they found that whereas the ratio is always *positive* when both *cored* carbons are used, it is *negative* for *solid* carbons.

If a perfectly steady current direct arc between *solid* carbon electrodes be shunted with an oscillatory circuit consisting of a suitable condenser and self-induction in series, then alternating currents of constant amplitude will be maintained in the circuit composed of the condenser, the self-induction and the arc, these alternating currents will cause the current through the arc to vary, and the arc will give out a musical note. I have therefore called it the Musical Arc. This will not occur if an arc between *cored* carbons be used, because such an arc has not the requisite instability, or, if the resistance of the inductive coil and connections exceeds a certain critical value. In a previous paper I have shown † that the necessary conditions in order to convert direct into alternating current by means of the arc are:—

$$(1) \frac{\delta V}{\delta A}, \text{ must be negative.}$$

$$(2) \frac{\delta V}{\delta A}, \text{ must be numerically greater than the resistance of the}$$

\* Proceedings of the Physical Society, 1896, vol. 14, p. 307.

† Proceedings of the Institution of Electrical Engineers, 1901, vol. 30, p. 262.

shunt circuit (exclusive of the condenser, which should of course be very high).

Besides resistance, any other dissipation of energy such as hysteresis or eddy-currents, may, if sufficient, cause the arc to fail to produce its note, and for this reason the inductive coils used are preferably without iron cores.

The pitch of the note depends on the frequency of the alternating currents in the shunt circuit. If the resistance of the circuit is small, as it should be for the best results, the frequency of these currents may be calculated from Lord Kelvin's formula mentioned above

$$\text{Frequency} = \frac{1}{2\pi\sqrt{L.F.}}$$

where  $L$  is the self-induction and  $F$  the capacity in the oscillatory circuit shunting the arc.

In order to show that this formula is really obeyed, a constant self-induction was taken and a series of condensers calculated to produce the eight notes of an octave which were connected to a keyboard; to produce a second octave  $\frac{1}{4}$  of the self-induction was used in conjunction with the same condensers, with this arrangement popular airs were played on the arc.

In view of the great sensitiveness of the ear to small differences from true musical intervals, the fact that the notes produced by this set of calculated condensers was even approximately in tune, indicates that Lord Kelvin's law was closely obeyed.

Chords could not be played on the above-mentioned key-board, as owing to the same inductive coil being used for each note, the depressing of two or more keys simply put the condensers in parallel and produced a lower note. Several experiments were made to see if it were possible to make one and the same arc give out two notes at the same time by shunting it with two distinct oscillatory circuits. When the periodic times of the two oscillatory circuits had a simple ratio such as the octave, the arc would emit both notes together and form a chord, but the condition seemed to be unstable, the chord often changing to a sound which was neither one note nor the other.

To obtain loud results, several arcs in series should be used all shunted by the one oscillatory circuit. A very convenient arrangement for working on 200-volt mains is to use four arcs in two parallel circuits, each circuit consisting of two arcs and a steadying resistance in series; by this means the four arcs, though supplied with power in two parallel circuits from the mains, will be metallically connected in series, and may be thus all four shunted by one oscillatory circuit.

A method of still further increasing the sound, first shown me by Professor Slaby, is to shunt the main condenser by a condenser consisting of alternate loose sheets of paper and tin-foil. In this case a loud note due to the alternating current is produced by the loose paper condenser as well as the note by the arcs.

It must not be forgotten that the arcs are ordinary *direct* current arcs between *solid* carbon electrodes which are taking energy from the direct current supply and converting it automatically without any moving machinery into energy in the form of alternating currents in the oscillatory circuit shunting the arcs. The frequency of this alternating current can be easily varied over a very wide range. I have already mentioned the range of two octaves which gave alternating currents having frequencies from 545 to about 2200 periods per second, and higher frequencies up to a limit of about 10,000 periods per second were easily obtained. No lower limit has yet been found, frequencies down to 170 having been used, or a range of just under six octaves. In order to produce the lowest frequency, a self-induction of about 0.15 henry and a capacity of six microfarads was used; under these circumstances it was found that although the arcs were only supplied from 200-volt direct-current mains, the alternating voltage between the terminals of the condenser sometimes reached nearly 2000 volts.

When the musical arc was first set up at the Central Technical College, where all the experiments were originally devised, an interesting observation in connection with the sensibility of the arc as a telephone receiver was made. It was noticed that an arc in Sir W. de W. Abney's laboratory played tunes, and this was found to be due to the fact that my musical arc and the arc in Sir W. de W. Abney's laboratory were supplied from the same street mains. Although his arc was not specially adjusted to a sensitive condition, and in spite of the two arcs being in separate buildings, 400 yards apart in a straight line, and at a considerably greater distance if measured along the mains, yet the sensibility of the arc was such that whenever tunes were played on the musical arc, they could be distinctly heard in Sir W. de W. Abney's laboratory.

The conversion of direct current into alternating current by means of the musical arc, besides being of scientific interest, forms a very convenient means of obtaining alternating currents, with which a large number of well-known experiments may be easily performed.\* It has, however, two further advantages, namely, that the frequency can be easily adjusted to any required value, and that the frequency is at once self-evident from the note the arc is giving out.

The comparison of the capacity condensers and the self-induction of coils can be easily made by comparing the pitch of the notes produced when they are used in the circuit shunting the arc. The effect of closed secondaries and cores on the apparent self-induction of coils is also very striking. The Elihu Thomson experiment of the repulsion of a ring by a coil carrying an alternating current obtained from the musical arc can be easily performed.

If the primary of an induction coil (the contact maker being put

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\* W. Peukert, *Elektrotechnische Zeitschrift*, 1901, p. 467.

out of action) be used as the self-induction in the shunt circuit, then a high frequency flame discharge can be obtained from the secondary. Using a spark gap and Tesla coil in the ordinary way and supplying it from the secondary of the above induction coil all the ordinary Tesla phenomena can be produced. This experiment is of scientific interest, in that, without the use of a high frequency alternator or of any mechanically moving parts, low voltage direct current is converted in two steps into high voltage and very high frequency Tesla currents. Each step consists of the use of an electrically unstable conductor, the arc in one case the spark in the second, in conjunction with a circuit in which oscillations can take place. The first step converts the harmless direct current into dangerous high potential current; the second step of the transformation, by still further raising the voltage and the frequency, again renders it harmless to human beings.

Magnetic space telegraphy can be very well demonstrated by using the self-induction coil in the oscillatory circuit as the transmitter. The effect of tuning the receiving circuit to the same note as the transmitter can be well illustrated. For instance, if a small incandescent lamp be used as the indicator in the receiving circuit, it is easy to so tune it to correspond with one note in the octave that the lamp will light up brightly when this note is sounded, will only just glow red if the next note higher or lower is depressed, and will not light at all for any other note; so that if a scale or tune be played on the musical arc, the lamp in the receiving circuit will light up brightly every time the note occurs to which the receiving circuit is tuned. It would be quite easy to tune a separate receiving circuit to each of the notes of the octave and so form a system of syntonised wireless telegraphy on a small scale.

There is no doubt that the commercial success of wireless telegraphy will largely depend on the perfection of the syntony which can be maintained between the transmitting and receiving stations, as the more perfect the syntony the larger the number of messages which will be able to be transmitted simultaneously, and the longer the distance over which they will be able to be transmitted. So long as the transmitter only sends out trains of waves of decreasing amplitude at regular intervals, as at present, no very perfect syntony can be hoped for. As soon, however, as the transmitter can be supplied continuously with high voltage, high frequency currents of constant amplitude and thereby caused to send waves of a definite constant frequency and amplitude, so soon will very accurate syntony become possible and a great advance in wireless telegraphy and transmission of energy be made. May not the principle of the musical arc render this possible in the future?

Friday, March 7, 1902.

SIR WILLIAM CROOKES, F.R.S., Honorary Secretary  
and Vice-President, in the Chair.

Professor H. BEQUEREL, D.O.L. Ph.D., Membre de l'Académie des  
Sciences, Paris, *Hon. Mem. R.I.*

*Sur la Radio-activité de la Matière.*

LA propriété que possèdent certains corps d'émettre un rayonnement invisible et pénétrant, était inconnue il y a six ans. Le mouvement d'idées que suscitérent les expériences de Röntgen conduisit à rechercher si la matière n'émettrait pas de semblables radiations, et l'on pensa d'abord au phénomène de la phosphorescence qui réalisait un mode connu de transformation et d'émission d'énergie. Cette idée ne devait pas s'appliquer au phénomène qui nous occupe, mais elle fut cependant féconde. Elle conduisit à choisir parmi les corps phosphorescents, les sels d'uranium dont la constitution optique est remarquable par la série harmonique des bandes de leurs spectres d'absorption et de phosphorescence. C'est en expérimentant avec ces corps que j'ai vu, en 1896, le phénomène nouveau dont je me propose de vous entretenir.

Voici, reproduites par la méthode de Lippmann, les lamelles de sulfate double d'uranium et de potassium qui ont servi aux premières expériences. Après avoir posé une de ces lamelles sur le papier noir qui enveloppait une plaque photographique, et l'avoir laissée ainsi pendant quelques heures, j'ai observé, en développant la plaque, que le sel d'uranium avait émis des rayons actifs, traversant le papier noir, ainsi que divers écrans interposés entre le corps rayonnant et la plaque (lamelles minces de verre, d'aluminium, de cuivre).

Je ne tardai pas à reconnaître que le phénomène était indépendant de la phosphorescence, et même de toute excitation de nature connue, telle qu'une excitation lumineuse ou électrique, ou une variation très notable de température.

On était donc en présence d'un phénomène spontané, d'un ordre nouveau. L'absence de cause excitatrice connue sur un produit préparé depuis plusieurs années dans le laboratoire, permettait de penser que le phénomène eût été le même à quelque moment qu'on l'eût observé; il devait donc paraître permanent, c'est à dire qu'il ne devait pas manifester un affaiblissement appréciable pendant un temps très long. C'est en effet ce que j'ai pu vérifier depuis six ans. Je mets sous vos yeux la première épreuve qui m'a révélé la spontanéité du rayonnement; celui-ci a traversé le papier noir qui enveloppait la

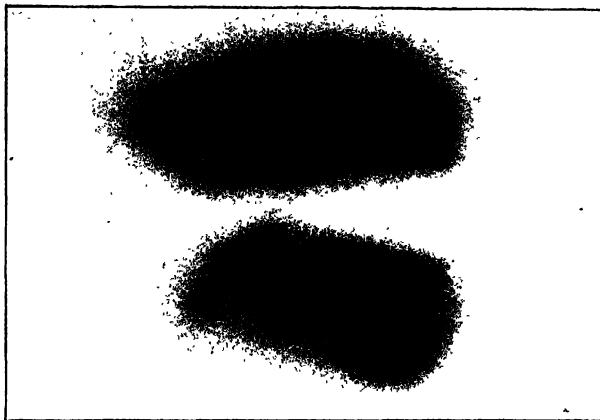


FIG. 1.

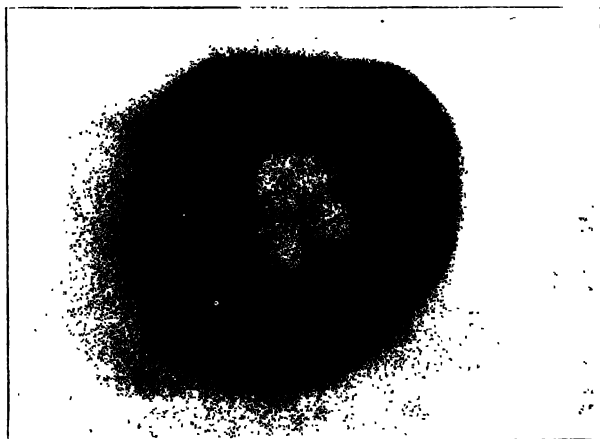


FIG. 2.

plaque, et une lame mince de cuivre en forme de croix (Fig. 1). Voici encore la radiographie faite à la même époque, d'une médaille en aluminium (Fig. 2); l'absorption inégale par les différentes épaisseurs du métal a fait apparaître l'effigie.

Dès la première observation, j'ai reconnu que le rayonnement nouveau déchargeait à distance dans l'air, les corps électrisés, phénomène qui donne une seconde méthode pour étudier ces rayons; la méthode photographique est surtout qualitative, l'électromètre fournit des éléments numériques de comparaison.

Au cours de ces premières constatations, je fus détourné de la voie dans laquelle les expériences ultérieures devaient me ramener, par plusieurs faits dont le principal est le suivant: Ayant protégé une plaque photographique par une plaque d'aluminium de 2 mm. d'épaisseur, et ayant disposé sur l'aluminium divers échantillons de poudres phosphorescentes, reposant sur des lamelles de verre et recouvertes de petits tubes en forme de cloche, comme le montre la figure ci-contre (Fig. 3), l'épreuve obtenue au bout de 48 heures de pose, et que je mets sous vos yeux (Fig. 4), donna des silhouettes des lamelles de verre telles qu'elles eussent été produites par la réfraction et la réflexion totale de rayons identiques à ceux de la lumière, mais qui auraient traversé les 2 mm. d'aluminium. Cette épreuve est unique: je n'ai pu la reproduire ni obtenir d'action avec le même échantillon de sulfure de calcium, ni avec aucune autre préparation phosphorescente. A la même époque M. Niewogłowski avait obtenu une impression avec du sulfure de calcium, et M. Troost avec de la blende hexagonale. J'ignore encore la cause de l'activité de ces produits, et de sa disparition. Ces faits et quelques autres m'avaient conduit à penser que le nouveau rayonnement pouvait être un mouvement transversal de l'éther analogue à la lumière; l'absence de réfraction et un grand nombre d'autres expériences me firent abandonner cette hypothèse.

Dans cette même année 1896, je reconnus que tous les sels d'uranium émettent des radiations de même nature et que la propriété radiante est une propriété atomique liée à l'élément uranium; les mesures électriques me montrèrent que l'uranium métallique était environ trois fois et demie plus actif pour ioniser l'air, que ne l'est le sulfate double d'uranium et de potassium. La même méthode permit d'étudier le rôle des gaz dans le décharge, de reconnaître qu'une sphère d'uranium électrisée conserve sa charge dans le vide, tandis que, dans l'air, elle se décharge. La vitesse de la chute du potentiel est sensiblement proportionnelle au potentiel si celui-ci est de quelques volts; elle devient constante et indépendante du potentiel pour les potentiels très élevés. Le gaz rendu conducteur par le rayonnement conserve cette propriété pendant quelques instants. Entre deux conducteurs maintenus à des potentiels constants le rayonnement établit, dans l'air, un courant continu.

Ces expériences ont été reprises et variées en 1897 par Lord Kelvin, puis par MM. Beattie et S. de Smolau. En 1897 Mr.



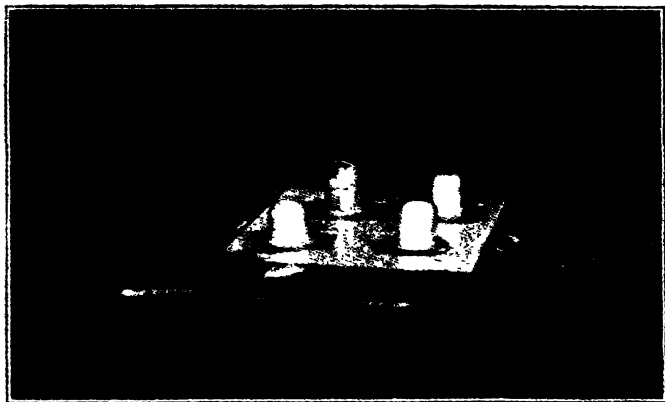


FIG. 3.

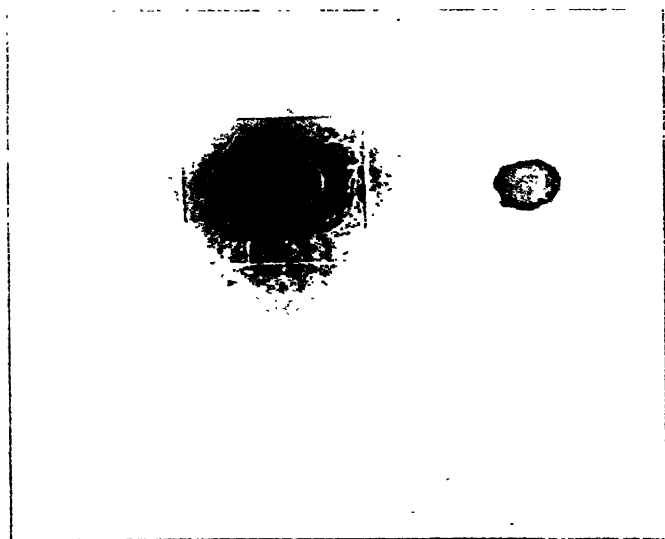


FIG. 4.

Rutherford montra comment les phénomènes dus à la conductibilité communiquée aux gaz par l'uranium, et l'existence d'un maximum dans le courant produit, peuvent s'expliquer dans l'hypothèse de l'ionisation à laquelle les beaux travaux de Mr. J. J. Thomson ont donné tant d'autorité.

En 1898, M. Schmidt et Mme. Curie observèrent séparément que le thorium a des propriétés analogues à celles de l'uranium, propriétés qui furent étudiées en particulier par Mr. Owens et par Mr. Rutherford. Mme. Curie, ayant mesuré l'activité ionisante d'un grand nombre de minéraux contenant de l'uranium ou du thorium, signala ce fait remarquable que plusieurs minerais étaient plus actifs que l'uranium métallique. M. et Mme. Curie en conclurent qu'il devait exister dans le minerai un corps plus actif que l'uranium ; et ils entreprirent de l'isoler. Traitant alors l'un des plus actifs de ces minerais, la pechblende de Joachimsthal, ils en séparèrent d'abord du bismuth actif auquel ils donnèrent le nom de Polonium, puis peu après du baryum très actif, contenant un élément nouveau, le Radium.

Ces produits se préparèrent par des précipitations fractionnées pour lesquelles on est guidé par les indications de l'électromètre ; l'activité des produits obtenus a dépassé 100,000 fois celle de l'uranium. Vers la même époque M. Giesel est parvenu à préparer des substances très actives, et, en 1900, M. Debierne a annoncé l'existence d'un nouvel élément, l'Actinium, sur lequel on a jusqu'ici peu de renseignements. De ces diverses préparations le radium seul est caractérisé comme élément nouveau ; il possède un spectre d'émission formé de lignes qui n'appartiennent à aucun autre corps connu, et le poids atomique des sels de baryum radifères augmente avec leur teneur en radium.

Le rayonnement de l'uranium était trop faible pour exciter la phosphorescence des corps. M. et Mme. Curie observèrent ce phénomène avec les rayons du radium ; bien plus les sels de radium se rendent lumineux eux-mêmes ; leur luminosité, comme leur rayonnement, est spontanée. Le rayonnement du radium produit des actions chimiques diverses, colore le verre, transforme l'oxygène en ozone, le phosphore blanc en phosphore rouge ; il ionise non seulement le gaz, mais encore les liquides (pétroles, air liquide) et les solides isolants, tels que la paraffine, en développant dans ce dernier corps une conductibilité résiduelle qui dure fort longtemps après que le rayonnement a cessé d'agir. Il provoque sur les tissus organiques des brûlures profondes analogues à celles que font les rayons X.

L'échantillon de radium que M. Curie m'a prêté pour cette conférence, me permet de vous montrer quelques-uns de ces phénomènes : ionisation de l'air, luminosité, phosphorescence.

J'ai constaté par l'épreuve photographique que je montre ici (Fig. 5), que le rayonnement du polonium ne traversait pas une mince feuille de papier noir qui formait un petit cylindre fermé par de l'aluminium ou du mica, et au fond duquel était la matière pulvérulente ; le rayonnement du radium traverse facilement cette en-

veloppe : nous verrons qu'il existe entre les deux rayonnements, des différences encore plus profondes.

Le rayonnement du radium redonne à certains cristaux et au verre la propriété d'être phosphorescent par la chaleur, quand ces corps l'ont perdue par une élévation de température préalable.

Les phénomènes d'absorption étudiés soit par la photographie, ou par la phosphorescence, ou par l'ionisation de l'air, avaient montré l'hétérogénéité du faisceau de radiations émises. Une observation nouvelle vint élargir le champ de ces recherches.

Vers la fin de l'année 1899, M. Giesel, puis MM. Meyer et Schweidler observèrent que le rayonnement de préparations actives était dévié par un champ magnétique, comme le sont les rayons cathodiques. De mon côté, à la même époque, sans avoir eu connaissance de ces expériences, je faisais la même observation avec le rayonnement du radium. On peut opérer de la manière suivante : Sur une plaque photographique enveloppée de papier noir, et placée horizontalement entre deux pôles d'aimant, on dépose une petite caisse en papier contenant quelques grains de matière active : le rayonnement est tout entier rejeté sur la plaque, d'un seul côté.

Presque aussitôt, je reconnus que les rayons du polonium ne sont pas déviés, et, par suite, qu'il existe deux espèces de rayons, les uns déviables et les autres non déviables. M. et Mme. Curie firent une étude électrique qui leur montra la présence simultanée des deux espèces de rayons dans le rayonnement du radium, leur inégale perméabilité variable avec la distance des écrans absorbants. L'épreuve photographique ci-jointe (Fig. 6) montre les deux espèces de rayons avec le radium ; j'ai reconnu récemment que la radiation du thorium comprenait les deux espèces de rayons, et que l'uranium émettait uniquement des rayons déviables, sous la réserve de l'existence de rayons non déviables beaucoup moins actifs. Il existe en effet une troisième espèce de rayons, qui ne sont pas déviables mais sont extrêmement pénétrants ; ils ont été plus particulièrement mis en évidence par M. Villard.

Ainsi le rayonnement des corps radio-actifs comprend trois espèces de rayons : des rayons déviables par un champ magnétique qui paraissent identiques aux rayons cathodiques ; des rayons non déviables de deux sortes, les uns très absorbables, les autres qui ressemblent à des rayons X très pénétrants. L'uranium émet surtout la première espèce, le polonium n'émet que la seconde, et le radium émet les trois à la fois.

Revenons aux rayons déviables. On peut leur appliquer la théorie matérielle édifiée par Sir W. Crookes et Mr. J. J. Thomson, et l'on en vérifie les conséquences avec la plus grande facilité. Dans un champ magnétique uniforme les trajectoires perpendiculaires au champ sont des circonférences de rayon  $\rho$  qui ramènent le rayonnement au point d'émission. Pour une émission oblique faisant l'angle  $\alpha$  avec le champ les trajectoires sont des hélices qui s'enroulent sur des cylindres de rayon  $\rho \sin \alpha$ . En plaçant sur une plaque photo-

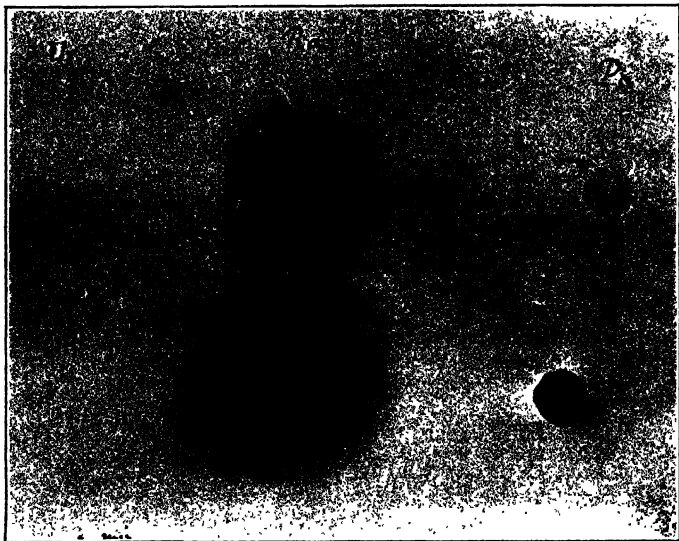


FIG. 5.



FIG. 6.

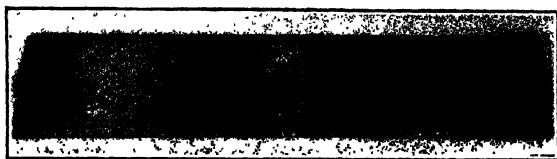


FIG. 7.

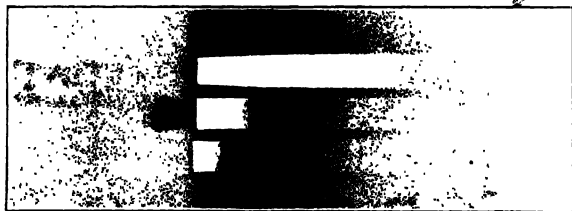


FIG. 8.

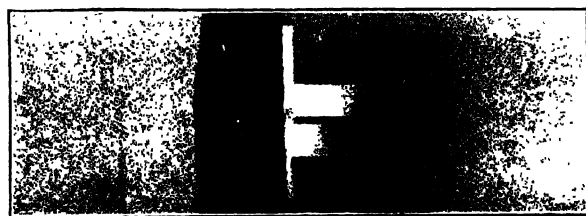


FIG. 9.

graphique horizontale parallèle au champ uniforme une petite cuve en plomb contenant quelques grains de baryum radifère et formant une source de très petite diamètre, le rayonnement est ramené sur la plaque et l'impressionne d'un seul côté ; un faisceau de rayons simples émis dans le plan normal à la plaque et parallèle au champ, doit figurer théoriquement un arc d'ellipse dont les axes sont dans le rapport des nombres 2 et 7. L'épreuve ci-contre (Fig. 7) montre ces arcs théoriques, obtenus en renversant le sens du champ, l'un dans l'air, l'autre dans le vide, sur une plaque enveloppé de papier noir ; l'intensité du champ magnétique était environ 4000 unités C.G.S.

Si l'on n'enveloppe pas la plaque photographique, et si l'on dispose sur celle-ci diverses bandes de papier ou de métal, formant écrans, on observe dans l'impression du rayonnement dispersé par le champ magnétique, des sortes de spectres d'absorption. À chaque trajectoire de courbure différente, correspondent des rayons de vitesses différentes qui ont des pouvoirs de pénétration différents.

Voici un exemple de ces épreuves, obtenu dans un champ de 1740 unités C.G.S. environ ; les écrans sont une bande de papier noir, une bande d'aluminium de 0,10 mm. d'épaisseur, et une bande de platine de 0,03 mm. d'épaisseur (Fig. 8). Pour avoir un spectre pur tel qu'en chaque point de la plaque il n'arrive qu'un faisceau dont les trajectoires aient la même courbure, on doit assujettir le rayonnement issu de la source ponctuelle à passer par un trou étroit. Le résultat est le même que le précédent comme le montre la figure ci-contre (Fig. 9). Celle-ci fait encore voir une impression très intense, due à des rayons secondaires provoquées par les rayons qui étaient arrêtés par une gouttière de plomb recouvrant la source, et dans laquelle était pratiquée l'ouverture qui donnait passage au spectre pur.

L'absorption varie avec la distance des écrans à la source radiante, et des rayons qui sont arrêtés par un écran placé sur la plaque peuvent traverser ce même écran lorsque celui-ci est interposé sur leur trajet, près de la source.

Ces expériences laissaient peu de doutes sur l'identité du rayonnement déviable et des rayons cathodiques. Cependant, il était nécessaire de démontrer qu'ils transportent des charges d'électricité négative, et qu'ils sont déviés par un champ électrique.

M. et Mme. Curie, dans une très belle expérience, ont montré que les rayons du radium chargent négativement les corps que reçoivent le rayonnement, et que la source se charge elle-même positivement. Pour cette double expérience il est nécessaire que tous les conducteurs et la source elle-même soient enveloppés complètement de matières isolantes telles que la paraffine. Pour la préparation active étudiée, la charge était de  $4 \cdot 10^{-13}$  unités C.G.S. par centimètre carré de surface radiante et par seconde.

De mon côté je suis parvenu à mettre en évidence et à mesurer la déviation électrostatique en projetant sur une plaque photographique l'ombre déviée d'un écran plan perpendiculaire au champ.

L'un des appareils est figuré ci-contre (Fig. 10) ainsi que l'une des épreuves obtenues (Fig. 11), dans laquelle sur les deux moitiés d'une même plaque apparaissent les ombres déviées correspondant au renversement du champ électrique, dont l'intensité était environ  $1,02.10^9$ .

L'hypothèse balistique attribue ces phénomènes à l'existence de masses matérielles transportant des charges d'électricité négative avec une vitesse considérable. Soit  $m$  la masse matériel d'une particule,  $e$  sa charge,  $v$  sa vitesse. On sait que dans un champ magnétique d'intensité  $H$  le rayon de courbure  $\rho$  de la trajectoire circulaire est donné par la relation

$$H\rho = \frac{m}{e} v.$$

La valeur numérique du produit  $H\rho$  peut servir à caractériser la nature de chaque rayon simple. D'autre part, dans un champ électrique d'intensité  $F$  le paramètre de la trajectoire parabolique est

$$\frac{m}{e} \frac{v^2}{F}.$$

La connaissance de ces deux grandeurs donne  $\frac{m}{e}$  et  $v$ . Pour une valeur de  $H\rho = 1600$  j'ai obtenu approximativement  $v = 1,6.10^{10}$  et  $\frac{m}{e} = 10^7$ . Ces nombres sont tout à fait de l'ordre de grandeur de ceux auxquels conduisent les mesures faites avec les rayons cathodiques, les considérations théoriques relatives à l'expérience de Zeeman et les déterminations de M. Lenard sur l'émission provoquée par les rayons ultraviolets.

Des nombres ci-dessus on déduit que par le fait du rayonnement déviable considéré il s'échapperait par chaque centimètre carré de surface radiante 1,2 mgr. matière en un milliard d'années.

En étendant ces mesures à des rayons de diverses natures et bien déterminés, on doit reconnaître si le rapport  $\frac{e}{m}$  est constant ou variable d'un rayon à un autre, et si ceux-ci ne diffèrent pas uniquement par leur vitesse: je n'ai pas terminé les expériences que j'avais entreprises pour résoudre cette question fondamentale, mais récemment M. Kaufmann s'est proposé de l'élucider. Il a combiné à angle droit l'action magnétique et l'action électrique; malheureusement l'expérience qui est difficile, ne lui a donné qu'une seule plaque bonne à mesurer. Pour des valeurs de  $H\rho$  comprises entre 1800 et 4600, il a trouvé que le rapport  $\frac{e}{m}$  variait de  $1,3.10^7$  à  $0,6.10^7$ , et la vitesse  $v$  de  $2,3.10^{10}$  à  $2,8.10^{10}$ .

La constatation d'une variation régulière dans le rapport calculé  $\frac{e}{m}$  a une importance théorique considérable: si ce rapport était

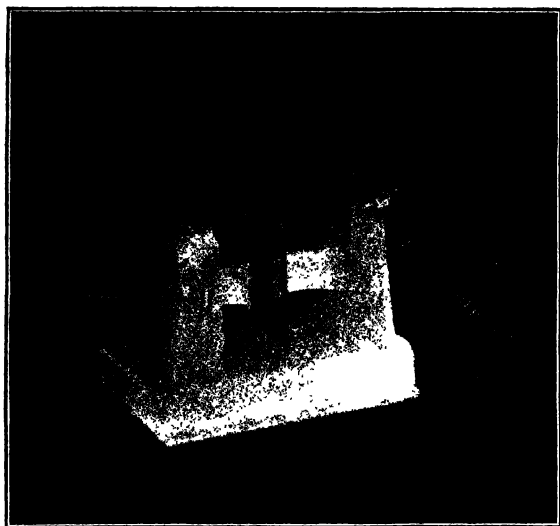


FIG. 10.

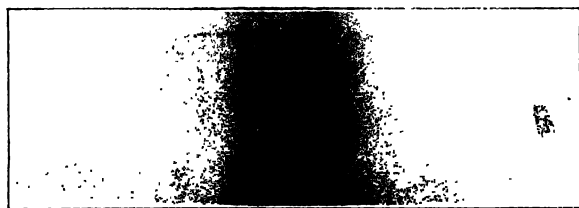


FIG. 11.



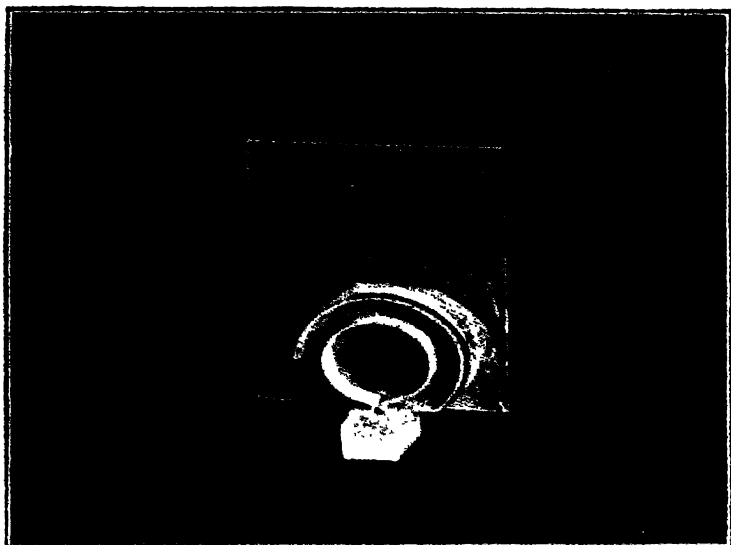


FIG. 12.



FIG. 13.

constant comme cela semblait résulter d'un grand nombre de mesures, on devrait en conclure que les rayons peu déviables pour lesquels le produit  $H\rho$  dépasse 5000, ont des vitesses notablement supérieures à celle de la lumière.

D'autre part, des considérations théoriques ont fait penser que la vitesse ne pouvait dépasser celle de la propagation des perturbations électro-magnétiques, c'est à dire la vitesse de la lumière, et l'on a été conduit à considérer les masses mobiles dans un champ magnétique comme douées d'une inertie particulière fonction de la vitesse. Dans ces conditions, la masse calculée devrait être, en partie au moins, apparente, et grandir indéfiniment à mesure que la vitesse réelle s'approche de celle de la lumière. Les nombres publiés par M. Kaufmann sont conformes à cette hypothèse.

Une autre conséquence de cette manière de voir, serait qu'il devrait y avoir continuité entre les rayons déviables et ceux qui ne le sont pas, car le rayon de courbure des trajectoires devient infini en même temps que la masse apparente.

L'épreuve photographique déjà mentionné (Fig. 6), ainsi que l'une des épreuves suivantes (Fig. 13), manifestent au contraire une discontinuité bien nette, et, dans la seconde épreuve en question, la pose a été assez prolongée pour que l'impression des rayons les moins actifs tels que les rayons pénétrants non déviés, soit nettement visible.

Cette épreuve a été obtenue en employant le dispositif suivant : Dans le champ magnétique uniforme, d'un aimant permanent on dispose normalement au champ une plaque photographique, puis on applique sur celle-ci des écrans formés de lames de plomb fixées sur une lame de verre comme l'indique la figure ci-contre (Fig. 12). Ces écrans sont percés d'ouvertures en forme de fentes plus ou moins profondes, normales à la plaque, et destinées à limiter les faisceaux étroits ; sur le trajet de ces faisceaux on peut disposer par le même procédé des écrans, tels que des lames d'aluminium. Au-dessous de la plaque, en regard d'une fente étroite pratiquée dans une lame de plomb, on place un petit bloc de plomb contenant une rainure profonde normale à la plaque, et dans laquelle on met la matière radiante. On a ainsi une source linéaire étroite, normale à la plaque, et de quelques millimètres de longueur. La rainure est recouverte d'une lame mince d'aluminium pour arrêter les rayons lumineux.

L'impression représente une section faite normalement au champ, du faisceau dont une partie est déviée. Chaque faisceau, correspondant à une vitesse déterminée, donne une impression sensiblement circulaire comme si le trajectoire entière était marquée sur la plaque. Dans ces épreuves, l'intérieur des cylindres crénelés formant les écrans est très fortement impressionné par l'émission secondaire du plomb. La première épreuve (Fig. 13) montre que par chaque ouverture il passe une infinité de rayons constituant des portions de spectres purs. Ceux-ci rencontrent une lame d'aluminium de 0,1 mm. d'épaisseur, et la traversent sans déviation, mais inégalement bien. Les rayons peu déviés sont pénétrants, et excitent des rayons secon-

dares à leur sortie de l'aluminium. Les rayons très déviables sont arrêtés, et font naître aux points frappés un rayonnement secondaire intense. Une seule des deux catégories de rayons non déviables apparaît sous la forme de deux lignes fines à l'opposé de la source ; ce sont les rayons très pénétrants. Les autres avaient été arrêtés près de la source.

La deuxième épreuve (Fig. 14) montre des faisceaux simples obtenus par une double série d'ouvertures. Par l'une d'elles il peut parfois passer deux trajectoires distinctes. Cette épreuve montre la transmission de rayons simples au travers de l'aluminium, et les effets secondaires qu'ils provoquent.

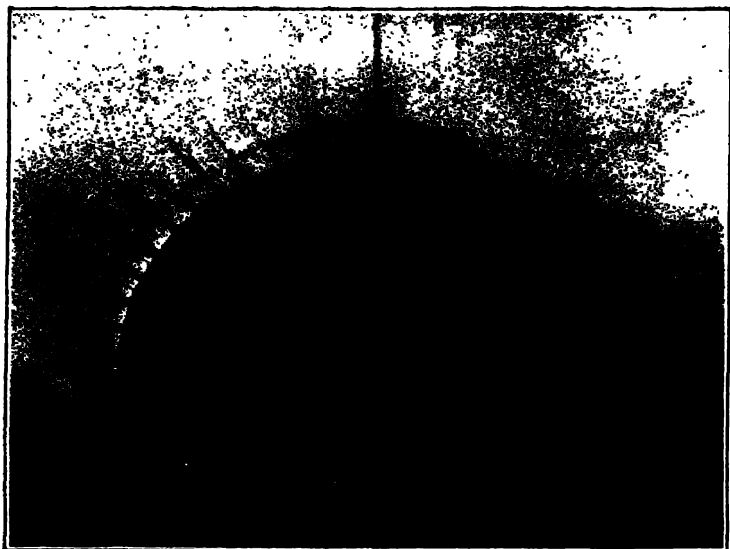
Le même procédé a permis de constater que les rayons secondaires étaient eux-mêmes déviables par le champ magnétique, dans le même sens que les rayons excitateurs.

Le rayonnement du radium comprend une partie très pénétrante formée des rayons les moins déviables et de rayons non déviables dont les propriétés semblent les mêmes que celles des rayons de Röntgen. Ces rayons pénétrants ne sont que très peu absorbés, et par suite leur action sur une plaque photographique ou sur l'air est très faible, de sorte que l'on ne peut, par les méthodes précédentes, avoir une idée exacte de leur intensité. Si l'on interpose sur leur trajet un écran très absorbant, ils le traversent partiellement, mais ils s'y transforment en partie en rayons plus absorbables. Cette transformation rappelle celle de la fluorescence, et par suite de l'action secondaire, l'effet, immédiatement derrière l'écran, est plus fort que si celui-ci n'existait pas. Une plaque photographique recevant le rayonnement filtré au travers d'une épaisseur de plomb de 1 cm. s'impressionne plus sous une plaque de plomb de 1 mm. d'épaisseur que dans les régions non recouverte par cet écran. L'épreuve ci-contre (Fig. 15) montre l'effet du rayonnement qui sort des parois d'une cuve de plomb après avoir traversé 5 à 12 millimètres de métal.

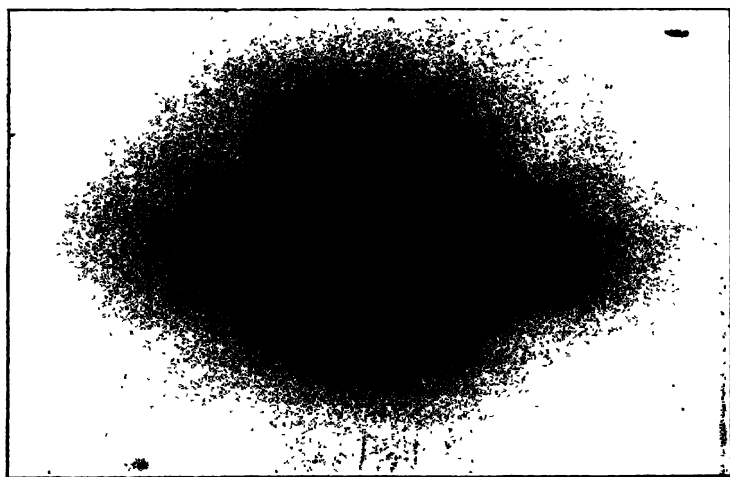
Ces phénomènes secondaires peuvent rendre compte en partie, des apparences d'ombres portées qui donnent les bords de tous les écrans plus ou moins transparents placés sur les plaques photographiques.

Tous les faits qui viennent d'être exposés sont exclusivement relatifs au rayonnement obscur qui traverse les corps opaques, les métaux, le verre, le mica ; mais il existe un phénomène tout différent, dont les effets sont arrêtés par le verre et par le mica, et sont comparables à ceux que produirait une vapeur d'une nature particulière. Ce phénomène fut découvert en 1899, simultanément par Mr. Rutherford et par M. et Mme. Curie.

Mr. Rutherford, en étudiant le rayonnement du thorium, vit qu'à côté de la radiation ordinaire, il y avait un effet produit par une "émanation," comparable à une sorte de vapeur ionisant l'air. Cette émanation se dépose sur les corps, principalement sur les corps électrisés négativement, et les rend momentanément radio-actifs. Mr. Rutherford fit sur ce phénomène de très intéressantes mesures.



**FIG. 14.**



**FIG. 15.**

En même temps M. et Mme. Curie découvraient que sous l'influence du radium les corps devenaient temporairement radio-actifs. Ce n'est pas l'effet secondaire décrit plus haut, c'est un phénomène persistant qui disparaît assez lentement à partir du moment où l'action du radium a cessé. M. Curie a appelé ce phénomène "la radio-activité induite," et il en fit une étude très complète; il a reconnu que le phénomène se produit avec une grande intensité dans un espace clos, que l'activité induite est la même sur tous les corps, et indépendante de la pression à l'intérieur de l'enceinte, mais que l'activation ne se produit pas si on maintient constamment le vide en enlevant les gaz produits; les solutions des sels de radium produisent le phénomène avec plus d'intensité que les sels solides. Les liquides, l'eau de cristallisation extraite des sels actifs, ou l'eau séparée d'une solution active par une membrane semi-perméable en cellulose, deviennent fortement radio-actifs. Il en est de même des gaz. Ces corps activés produisent les mêmes effets que le radium; ils émettent un rayonnement pénétrant qui traverse les enveloppes de verre qui les contiennent, et rendent celles-ci lumineuses. L'activité induite se propage de proche en proche dans le gaz d'une enceinte formée, même au travers de tubes capillaires et de fissures imperceptibles; les corps s'activent d'autant plus que le volume de gaz qui est en regard de leur surface est plus considérable. Les corps phosphorescents deviennent lumineux en s'activant.

Dans un récent travail, MM. Elster et Geitel ont reconnu que l'air atmosphérique présentait des propriétés analogues à celles des gaz activés, et M. Geitel a pu recueillir sur des fils électrisés négativement, des traces de produits radio-actifs. La cause de cette radio-activité est un problème d'un haut intérêt.

Enfin, il est un mode remarquable d'induction qui est de nature à inspirer les plus grandes réserves dans les conclusions que l'on peut formuler relativement à la présence d'éléments nouveaux dans les préparations radio-actives. Toute substance inactive que l'on introduit dans une dissolution d'un sel d'uranium ou de radium, et que l'on sépare ensuite par précipitation, est devenue radio-active, et perd lentement cette radio-activité. Ce fait a d'abord été observé par M. Curie et par M. Giesel qui a ainsi activé du bismuth. Avec l'uranium, une trace de baryum précipitée à l'état de sulfate devient notablement plus active que l'uranium; le baryum ainsi activé n'émet, comme l'uranium, que des rayons déviables.

Après cette précipitation, le sel d'uranium ramené à l'état solide est moins actif qu'auparavant; on peut même accentuer cet affaiblissement par des opérations successives, mais les produits reprennent, peu à peu, spontanément, leur activité première.

L'affaiblissement temporaire de l'activité à la suite d'une dissolution est un fait général pour les sels d'uranium et de radium.

Avec les sels d'actinium M. Debierne a communiqué au baryum une activité très grande. Le baryum activé peut se séparer du baryum inactif; il se fractionne comme le chlorure de baryum radi-

fère, les parties les plus actives étant les moins solubles dans l'eau et l'acide chlorhydrique. M. Debierne a obtenu ainsi un produit mille fois plus actif que l'uranium. Le baryum activé se comporte donc comme un faux radium, mais il diffère du radium véritable par l'absence de spectre et parce qu'il perd son activité avec le temps.

Parmi les préparations radio-actives, un grand nombre pourraient être des corps activés. Tel est le cas du polonium qui est vraisemblablement du bismuth activé.

L'uranium et le radium sont caractérisés par leur spectres d'émission, et par la stabilité de leur radio-activité. L'accroissement spontané que l'on observe sur les sels déposés des dissolutions, pourrait trouver une explication dans un phénomène d'auto-induction des molécules actives sur les molécules inactives qui leur sont associées.

L'origine de l'énergie rayonnée par les corps radio-actifs est toujours un énigme. Dans l'hypothèse matérielle, il ne paraît pas invraisemblable d'assimiler le phénomène à l'évaporation d'un corps odorant, de comparer l'émanation à une sorte de gaz dont les molécules auraient des masses de l'ordre de grandeur de celles des ions électrolytiques, et d'identifier le rayonnement à des rayons cathodiques provenant de la dislocation de ces ions et donnant en même temps une émission de rayons X. On imputerait ainsi la dépense d'énergie à la dissipation de la matière active. Bien que cette hypothèse rende à peu près compte de la plupart des faits, il n'existe aucune expérience précise qui lui donne une sanction.

Je ne puis m'étendre plus longuement sur ce sujet dont j'ai résumé très incomplètement l'état actuel, en insistant sur la partie physique qui est plus spécialement de mon domaine, et bien que la partie chimique ait donné lieu à des travaux du plus haut intérêt.

Ces questions ont fait naître des aperçus nouveaux sur les transformations de la matière. En dehors des conditions exceptionnelles dans lesquelles elles permettent d'étudier les rayons cathodiques, elles ont soulevé et soulèvent chaque jour des problèmes nouveaux, dont le premier et le plus mystérieux est la spontanéité du rayonnement.

[H. B.]

Friday, March 21, 1902.

GEORGE MATTHEY, Esq. F.R.S. Vice-President, in the Chair.

GEHEIMRATH PROFESSOR OTTO N. WITT, Ph.D. F.C.S., of Berlin.

*Recent Developments in Colouring-Matters.*

THE love of colour is innate in the human mind, and this alone, if nothing else, would be sufficient to account for the interest with which the coal-tar colour-industry has met from its beginning. In England especially its progress has been watched with great attention, and only two days ago the Vice-Patron of this Institution, His Royal Highness the Prince of Wales, has shown by some remarks, made in his Opening Address of the New Technical Institute at Bushey, that the interest taken in this subject has in no way abated.

Artificial colouring-matters have formed so often the subject of more or less popular lectures, and this subject has been treated with such ability by eminent scientists, that it becomes difficult to show this domain of chemistry in a light new and interesting to an audience such as I have to-day the honour to address. Many years ago you have seen in this room the early achievements of the newly-created industry, marvellous for their beauty and brilliancy. Later on the progress of this industry has been duly recorded. More recently still it has become the custom in this country to view colour-making not so much from its chemical or industrial side, as from the standpoint of the national economist, who contemplates the values produced by industrial enterprise, and investigates the reasons why these values should be unevenly distributed amongst the different nations, striving side by side for progress and engaged in friendly, yet none the less eager competition.

I may say at once, that I have no intention to treat my subject from either of these points of view. I take it for granted, that everybody is acquainted with the marvellous variety and brilliancy of artificial dye-stuffs, and I am too much of a chemist and too little of an economist to offer any original or valuable view about that side of the question which I have just mentioned. But I shall make an attempt to trace in this lecture the influence of the development of theoretical chemistry on the progress of the colour industry. If in so doing, I should refer now and then to theoretical points without being able to explain them in detail, I hope to be forgiven.

In beginning this lecture allow me briefly to refer to the history of it.

When I received from Sir William Crookes the flattering invitation to speak before you this evening, my thoughts naturally wandered back to some recollections in connection with this Institution. I remembered vividly several brilliant lectures to which I had the privilege of listening in this room, where the spirits of Davy and Faraday, of Graham and Huxley, of Würtz and of my immortal friend A. W. von Hofmann seem still to be hovering. I felt loth to raise my own voice in such hallowed precincts. But then I also remembered an almost forgotten episode in my own life, which I ask your permission to tell.

I remembered, that almost exactly five-and-twenty years before receiving this invitation, I, then a very young chemist, had read before the Chemical Society of London, a paper containing a then somewhat daring speculation on the connection of the constitution of colouring-matters with their properties, a paper which the Publication Committee refused to print. A lively discussion followed, which was wound up by some encouraging remarks from the president, the late Mr. De la Rue. He said, that he hoped, that this speculative paper would prove useful in clearing up the complicated domain of colouring-matters, and that perhaps on some future occasion I should be in a position to place before the world, in a *Royal Institution lecture*, the results which had been obtained by its help.

This strange reminiscence, coupled with the curious fact that Mr. De la Rue's prophetic words were fulfilled just when the period commonly assigned to a Jubilee had elapsed, gave me the courage to accept Sir William's kind invitation. For though I have done comparatively little towards the increase of our knowledge of colouring-matters, the five-and-twenty years past have sufficed to shed a brilliant light on what Mr. De la Rue could then justly call a very imperfectly known domain of chemistry, and innumerable facts brought to light during this period by a whole army of assiduous workers are now by common assent being classified under a theory which is neither more nor less than the suggestions contained in that rejected paper of mine, which I had fortunately published in another journal.

I may add, that I have been guilty in later times of another theory, which refers to the domain of dyeing, and which has still many opponents. This theory is the direct outcome of the theory of colouring-matters, and may be illustrated by some simple, yet striking experiments, some of which I intend to show you.

A fundamental question in the chemistry of dye-stuffs, and one not at all easy to answer, is this: "What is a dye-stuff?" Clearly it is something totally different from a substance only endowed with the power of selective absorption of light, a power which causes it to appear coloured. We know now that there are more substances in creation which possess this power than bodies which lack it. In this very room we have learned, that the air itself, through which the solar rays penetrate on to the surface of the earth, is blue and



not colourless, as we used to think. But even if we leave out of the question such faintly coloured substances as air and water, if we restrict our consideration to compounds endowed with a very intense power of selective absorption and at the same time soluble in the water which we employ for preparing our dye-baths, we do not arrive yet at the true definition of the dye-stuff. Cuprio salts, soluble chromates and many other intensely-coloured bodies are no dye-stuffs, as may be easily shown by experiment. Yet these compounds penetrate into the interior of textile fibres which are immersed into their solution. They must do so, according to the laws of Osmose so ably expounded by Thomas Graham, because they are crystalloids and the fibres are invariably colloids.

We know now that the laws of Osmose are identical with the laws governing solution, and that crystalloids are able to wander into the interior of colloids because they are soluble in their substance. Osmotic processes may be observed between two liquids which cannot be mixed with each other, just as well as between a liquid and a colloid immersed into it. Consequently we are justified in assuming that the same powers are at work in both cases.

In my first experiment (Exp. I.)\* I intend to show you that a crystalloid, dissolved in some liquid such as water, and brought into contact with another liquid, not miscible with the first, such as ether, will either remain indifferent to the ether altogether, or it will leave the water and wander into the ether, or it will be distributed according to a certain ratio between the two solvents. In this latter case we have reason to believe that a constant interchange of molecules takes place between the two solutions. Clearly, this will only happen if there exists no great difference in the solubilities of the crystalloid in water and in ether. In that case the water will continually abstract nearly as many molecules of the crystalloid from the ether as the latter will take up from the water, and thus an equilibrium will be reached. If, on the other side, there is a great dissimilarity in the solubility of the crystalloid in the two solvents, then this process of mutual interchange will become so one-sided that it practically amounts to the absorption of the whole of the crystalloid by one of the solvents.

My second experiment (Exp. II.)† is a more striking illustration of these fundamental facts. If we mix together two coloured solutions, one an aqueous one of a substance much more soluble in ether than in water, and the other an ethereal one of a substance more soluble in water than in ether, then the two solutions, on shaking, change colour, and their shades are reversed.

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\* Details of experiment: An aqueous solution of magenta does not yield its colouring-matter to ether; indophenol, on the contrary, is entirely taken up by ether. The dye-stuff, which is partly taken up by ether, is also a member of the indophenol group, the constitution of which is not yet fully established.

† The ethereal solution used contained magenta acetate, whilst the aqueous one was prepared with trichloro-indophenol.

According to my theory, the process of dyeing, considered so problematical by many experts in this ancient and useful art, is strictly analogous with this wandering of molecules governed by the laws of solution, which we can so easily observe and control in operating with two non-miscible liquid solvents.

In my next experiment (Exp. III.)\* we see that a dye-stuff wanders from the bath on to the fibre in much the same way as it wandered from water into ether. And if the fibre be previously dyed with a colouring matter little soluble in its substance, then this may be expelled and replaced by another of greater solubility. (Exp. IV.)\*

We see now that, in order to become a dye-stuff, a substance must not only be so intensely coloured that it can communicate its own shade to colourless substances holding it in solution; it must not only be soluble in water or any other liquid suitable for preparing a dye-bath; but it must also be soluble, and even much more soluble than in water, in the colloid, which forms the substance of the textile fibre. The finished dyed fabric is nothing more nor less than a solid solution of the dye-stuff in the substance of the fibre, unless there are secondary chemical influences, such as that of the mordants, at work, which change the solution into a suspension by precipitating the dye-stuff after its immigration into the fibre.

This peculiar combination of solubilities is very rarely met with amongst the coloured substances of an anorganic nature. In the vast domain of organic compounds of the aliphatic series we meet with very few dye-stuffs, because its members are mostly colourless, or but very faintly coloured. In the aromatic series, on the contrary, the power of selective absorption of light is so very frequent, that it would be very curious indeed if just that combination of solubilities, which is the making of the dye-stuff, were not of common occurrence. Taking as a basis the universally admitted axiom, that the physical properties of every compound are direct functions of its molecular constitution, we may easily believe that that peculiar combination of solubilities which I have shown to be the characteristic feature of the dye-stuff, would be the result of certain general conditions fulfilled in the constitution of many members of the aromatic group. My theory, proposed five-and-twenty years ago, was nothing else than an attempt to ascertain these general conditions by investigating the constitutional peculiarities of all those dye-stuffs the constitution of which had been fully established in those days.

I have no intention to tax your patience by explaining in detail the results of that old investigation. It will be sufficient to summarise them by saying that in the molecule of every colouring matter, the constitution of which has been ascertained to this day

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\* In Exp. III. wool was dyed with erythrosine in the ordinary way, whilst in Exp. IV. a cotton cloth, previously dyed with patent blue, was treated in a bath of Congo red.

(and there are many thousands of them), certain atomic constellations have been observed which seem to be essential, and of which always two must be present. One of these constellations is a group of atoms, which is the cause of the selective absorption of light. This group of atoms I call a *chromophore*. The number of atomic groups endowed with chromophoric properties amounts at present to about two dozen, and is being constantly increased by the progress of chemical research. All the chromophores, however, have that in common, that they are unable to exert their influence unless they are helped by the presence of another group of atoms, which I call the *auxochromic* group. Very few auxochromic groups are known, and they belong to those which occur most frequently in the whole domain of organic chemistry—the amino group in its various forms, the hydroxyl group occurring in all the phenols, the sulpho- and the carboxyl group. None of these will cause a substance to become a dye-stuff unless this substance also contain a chromophore, but the latter is equally helpless if deprived of the assistance of the auxochromic group. Thus we meet in the molecular world that condition of the necessity of mutual help and assistance between two heterogeneous forms, which we can also trace in Sociology, a fact the establishment of which will no doubt be greeted with satisfaction by the ladies in this audience.

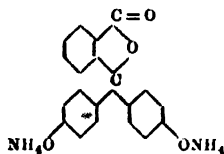
Our ideas on the nature and constitution of those groups which may act as chromophores have of course undergone many changes. Undoubtedly there must exist a law which governs the formation of chromophoric groups, but so far this law has not been definitely established. Some progress has, however, been made towards this end. At first the chromophores which we had gradually collected formed rather a motley crowd, and seemed to have no points in common. At present chemists working in this domain are inclined to attribute a quinoid structure to the great majority of colouring-matters. If this view be correct, then all these substances would be derivatives, not of benzene and its congeners, but of hydrocarbons containing two hydrogen atoms more in their molecule, derived from dihydrobenzene as a prototype. As sometimes it is almost impossible to decide in favour of one view or the other, the convenient hypothesis of tautomerism was resorted to, but in some cases we have been able to establish definitely the quinoid formula. Such is the case with the large and brilliantly-coloured group of dye-stuffs called phthaleines, which, according to modern view, must be considered as quinoid derivatives of benzoylbenzoic acid. The experiments which lead to this conclusion are so striking, that I cannot refrain from producing one of them, which has never been shown yet, though the time at my disposal does not allow its exhaustive discussion from a theoretical point of view. If we dissolve the well-known phenolphthaleine in anhydrous ether containing some ammonia, the solution is perfectly colourless, but if we add ordinary water to this solution (Exp. V.), it assumes a beautiful red coloration. This peculiar fact that water

alone is sufficient to cause the formation of this colour is perfectly incomprehensible if the old views on the constitution of phthaleines, which are still given in the majority of text-books, be adhered to, but it is exactly what we might expect to happen if we assume that the ammonium salt of phenolphthaleine possesses a cycloid constitution in its ethereal solution, and that it is isomerised into the quinonoid form by the addition of water.\*

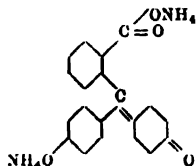
Thus our knowledge of the chemical causes of the physical properties of colouring-matters is continuously developing. Quite lately we have even begun to form definite views about the connection of the chemical constitution of aromatic substances with that peculiar form of selective absorption of light which we call fluorescence, and which has formed, from the physical point of view, the subject of the masterly investigations of Sir Gabriel Stokes. The phenomenon of fluorescence is very frequently met with in dye-stuffs, and in the raw materials used for their manufacture. It can be exhibited in a very striking way with the help of electricity, either by allowing an arrow of electric light to penetrate into the solution of a fluorescent substance or by working a Geissler tube of suitable shape submerged in such a solution (Exp. VI.). The fact that the fluorescence of many substances is chiefly caused by the ultra-violet light, I shall try to demonstrate by the following, somewhat delicate, experiment: I have here, submerged in a solution of cosine, a Geissler tube, the lower part of which is ground out of a piece of rock-crystal, whilst the upper half is made of glass. When the electric current passes this tube the fluorescence round the quartz part of it is stronger than that in the neighbourhood of the glass, because the latter absorbs a good deal of ultra-violet light, whilst the quartz is almost free from such absorption. (Exp. VII.)

An immense amount of patient work has been accomplished by many chemists in the hope of establishing definite views on the constitution of the azo-colours, that group of dye-stuffs the introduction of which into the colour-industry was the direct consequence of our early efforts to cast off empiricism, and to conduct our search for new colouring-matters according to definite scientific principles. Simple and transparent as the constitution of azo-colours appears to be if viewed superficially, yet it offers some problems of extraordinary

\* The isomerism of the two forms of the ammonium salt of phenolphthaleine is best explained by their constitutional formulæ:



*Cycloid Form.*



*Quinonoid Form.*

difficulty, which have not been solved so far. But fortunately these difficulties have in no way interfered with the technical development of this family of dye-stuffs, which has been for a whole quarter of a century one continued and unparalleled series of successes. The process for producing these dye-stuffs is of the greatest simplicity. It consists in pouring together (Exp. VIII.) cold aqueous solutions or suspensions of diazo-compounds and phenols or amines. The dye-stuff is formed at once in a state of absolute purity, and with a yield absolutely theoretical; it need only be collected and dried to form a saleable product. No wonder, then, that these dye-stuffs gradually became the leading ones, and to a great extent superseded the old empirical products which were concocted in many complicated operations, with yields very far from satisfactory. As the number of diazo-compounds and of phenols and amines at our disposal is very large, the number of dye-stuffs which may thus be prepared is quite extraordinary; it has been computed, according to the rules of permutation. 3,159,000 different individual dye-stuffs have thus been proved to be at present easily accessible to our industry. Of these at least 25,000 form the subject of German patent specifications and of corresponding specifications in England, France, the United States, and other countries. Over five hundred are regularly manufactured on the larger scale.

The prolific nature of the azo-colour-reaction explains the fact, that in this group we can choose, much better than in any other, substances possessing that ratio of solubilities in water and in the colloid substance of the various textile fibres, which we require. We can produce, quite at will, azo-dye-stuffs which dye wool or silk or cotton, which dye slowly or quickly, which will stand soap or acid or alkali. This possibility of adjusting the chemical properties of dye-stuffs with an almost mechanical precision has been the cause of one of the greatest successes of the colour-industry, the introduction of what is now known under the name of "substantive dye-stuffs," an expression which means dye-stuffs that will dye cotton and other vegetable fibres from a simple aqueous dye-bath without the use of any mordant. The difference of the solvent power of cellulose and of water is for the vast majority of dye-stuffs so small, that the process of dyeing vegetable fibres with these ordinary colouring-matters can only be compared to that case of the joint action of ether and water on some substance soluble in both these solvents, where an almost equal division of this substance takes place between the two solvents. Such cases exist, as you saw in the first experiment. It is amongst the azo-dyes that we have found compounds which are so much more soluble in cellulose than in water, that they readily leave their aqueous solution and take up their abode in the fibre. And we have not only found these dye-stuffs but also the law which governs this most valuable abnormal solubility: it appears in all azo-colours, which are prepared with diazo-compounds derived from symmetrical para-diamines. A novel and extremely fertile field for a systematic

search for new dye-stuffs was thus opened, a field which has occupied hundreds of busy workers for many years, many of whom carried home a rich reward.

But whilst this field bore its rich harvest, others were by no means neglected. The search for dye-stuffs, which will dye cotton without a mordant, could not make us forget that just those colouring-matters which imperatively demand the use of mordants are those which from times immemorial have been used in preference for the production of fast and lasting shades. The brilliant synthesis of alizarine by Graebe and Liebermann, which made the world ring with admiration early in the seventies, had given us ample proof that the old and to this day not wholly forgotten axiom, that there are two kinds of dyes: natural ones, which are fast, and artificial ones, which are fugitive, was a preconceived idea, totally devoid of any scientific foundation. The enormous financial success of the alizarine industry formed a tempting invitation to search for other dye-stuffs, which, similar to alizarine, would be endowed with the power of forming almost indestructible lakes with mordants of a sesquioxycic nature. Here too, like everywhere in science, we have marched for some time on the paths of empiricism, but here too logical deduction has come to our aid in disclosing the laws which govern the formation of lakes. In this case it is not (as in the substantive azo-dyes) the carbonic nucleus which determines the *physical* properties (viz. the ratio of solubilities) of the dye-stuff, but it is the peculiar position of the auxochromic groups contained in the molecule, which governs its chemical properties. We know now, that a dye-stuff must contain, in order to be able to form lakes with sesquioxycic mordants, two hydroxyl groups in juxtaposition. If this condition be fulfilled, the dye-stuff will dye in the same way and with equal fastness as alizarine, even if it be no derivative of anthracene, like the early alizarine dyes; and if these two hydroxyl groups or a suitable equivalent for them be missing it will lack all power of dyeing mordants, even though derived from anthracene. With this law once established the synthesis of mordant-dyestuffs became a very easy matter, and to-day there is hardly a group of colouring-matters in which there are not some members possessed of this peculiarity and owing it to the same uniform cause. Still the group of the oxyketones, to which alizarine itself belongs, remains the true home of mordant-dyes, but this group has grown to-day into a very numerous and varied one. Mordant-dyes of every shade are to be found in it, and cotton is no longer the only fibre to which such dyes are applied. It is a fact worthy of notice, that amongst the many dyes of this class which we now possess and the constitution of which is fully established there is not a small number, the molecule of which contains three, four, five or even six hydroxyl groups. Yet this increase of auxochromic groups does not influence in the least the behaviour of these dyes to mordants, this is only governed by the two hydroxyl groups in ortho-position, and any other such group

introduced into the molecule only changes the shade, not the characteristic chemical properties.

A greater variety still than by the achievements of modern synthetical work will come into this group of mordant-dyes by the progress of the elucidation of the constitution of the natural dye-stuffs occurring in roots, barks and woods. A good many of them are still unsolved mysteries, but there can be no doubt that they owe, like alizarine, purpurine and the other madder dye-stuffs, their property of dyeing metallic mordants to the presence of hydroxyl groups in ortho-position in their molecule.

A very large and varied group of colouring-matters, which for a long time resisted all attempts at unravelling their constitution, are the Saffranines, Eurhodines, Oxazines, Thionines, Indulines and other allied groups. They are now completely understood, and have been recognised as the amino- and oxy-derivatives of certain peculiar substances such as the azines and azonium-bases, the molecule of which possesses a ring-structure. Here no longer carbon atoms only form the closed chain, but nitrogen, oxygen and even sulphur atoms participate in its structure and bring about the peculiar properties of the compounds. When this fact was at first ascertained it seemed sufficient for the explanation of the behaviour of such compounds as dyes. It was only somewhat later on that we recognised that in these classes of dye-stuffs especially a quinonoid structure is essential.

The greatest and most brilliant success of the chemistry of dye-stuffs is however the industrial synthesis of indigo. This offers so many points of general interest, that I am sure to meet with your approval if I refer to it in some detail.

The indigo problem is one of the oldest problems of chemistry. When Baeyer took it up more than thirty years ago he found the ground well prepared by others who had worked before him. But his is the merit of having completely elucidated the constitution of this extraordinary product of nature. He and others have also shown various methods for the synthesis or artificial production of indigo. In the laboratories artificial indigo has been known for the last twenty years.

But in this case the scientific synthesis of a natural product proved to be by no means identical with the industrial one. Industrial methods can only enter into competition with nature if they work more economically than nature does. In the case of indigo there seemed to be little hope for fulfilling this condition. The most enthusiastic admirers of the modern synthetical industry could not help seeing that all evidence in our hands went against the probability of the practical synthesis of indigo, and just those who understood most of these things could least of all close their eyes to that fact. It could not be denied that every possible synthesis of indigo, those known as well as those which might still be expected, had to start from some aromatic derivative of benzene, containing one carbonic and one nitrogenous side-chain in ortho-position. Of

all the products at our disposal which fulfil that condition, ortho-nitrotoluene is the most easily accessible. Now, taking it for granted that indigo could be prepared regularly and with good yields from orthonitrotoluene, there still remained that difficulty, that all the toluene produced in the world, even if we suppose that all the other uses to which this hydrocarbon is put at present could be suppressed, would not suffice for the production of the world's consumption of indigo.

If, under such circumstances, the industry of artificial dye-stuffs continued to work at the indigo problem, it did so more for the general interest attached to it, and with a view to securing some of the finer applications of indigo in printing, than in the hope of being able to compete with the natural product in the great consumption of vat dyeing. If, on the other hand, the indigo planters in the far East showed but small apprehension of the danger of which they were occasionally warned, we cannot blame them for it; they had, no doubt, taken the advice of competent people, and these had told them what was correct according to the knowledge of the time.

The final result has shown all the calculations of experts to be wrong, but in such a way that they, too, can surely not be blamed for the error they committed.

The process by which indigo is at present manufactured on a colossal scale by the Badische Anilin- und Soda- Fabrik in Ludwigs-hafen on the Rhine, is based on Heumann's synthesis of this most important dye-stuff, which consists in submitting phenylglycine to a fusion with caustic alkali. Phenylglycine is prepared by the action of monochloracetic acid upon aniline. The yield of indigo obtained is a poor one, but it can be very much improved if, instead of phenylglycine, we take its orthocarbonic acid. In this we have again the presence of a nitrogenous and a carbonic side-chain in ortho-position. To prepare this acid we should have to start, according to the ordinary rules, from toluene, transforming it by a succession of operations. Thus we come again to toluene as a starting-point, and to the difficulty already explained.

There is, however, one somewhat abnormal process of preparing the same compound from phthalic acid. It consists in converting this into phthalimide, and treating the latter with sodium hypochlorite. By a somewhat complicated reaction, the nature of which need not be explained, one of the carboxyl groups of the phthalic acid is replaced by the amido group, anthranilic acid is formed, and this, if treated with monochloracetic acid, yields phenylglycine-carbonic acid, which has proved so important for the manufacture of indigo. Now phthalic acid is prepared by a powerful oxidation of naphthalene, and naphthalene again is that constituent of coal-tar which is present in by far the largest quantity.

It is true that the process for transforming naphthalene into phthalic acid, which was the only one known at the time when all these facts were first recognised, gave very bad yields, and was at the same time



costly. The whole indigo problem stood thus reduced to the problem of transforming naphthalene cheaply and economically into phthalic acid. This has been accomplished by the Badische Anilin- und Soda-Fabrik by heating naphthalene with fuming sulphuric acid in the presence of mercury salts. Torrents of sulphur dioxide escape, and the whole process can only be carried out properly if the means be given to convert this gas again into fuming sulphuric acid, which may be used again for treating fresh quantities of the hydrocarbon. The new sulphuric acid process of the Badische Anilin- und Soda-Fabrik has thus been of paramount importance for the working out of the indigo problem.

Some of the older synthetical methods of producing indigo are so easy and rapid that they can easily be shown as a lecture experiment. If, for instance, we add a caustic potash solution to a solution of orthonitrobenzoic aldehyde in acetone, indigo is formed at once and settles out in dark-blue crystalline flakes (Exp. IX.). The synthesis now in practical use is a little more delicate in its execution, but there are certain modifications of it which are rapid enough to be shown in a lecture experiment (Exp. X.).

The action of the alkali on the phenylglycine-carbonic acid does not at once produce indigo, a colourless derivative of the dye, indoxylcarbonic acid, or rather its potash salt, is formed at first, but if we dissolve this in hot water and introduce a current of air, it is at once and with a quantitative yield transformed into indigo which settles out in the shape of a crystalline deposit of infinitely fine division. This is collected in filter-presses and delivered into commerce in the shape of a paste or a powder.

The industrial synthesis of indigo is extremely interesting, because it is a triumph not wholly due to chemical science. Science has shown the way to success, but it was quite unable to clear away the difficulties arising from practical and economic considerations. Here the representatives of our great industry had to advance independently and on paths for which theoretical knowledge could not serve them as a guide. Unlimited praise and admiration is certainly due to them for the masterly way in which they grappled with colossal difficulties and for the courage with which they staked millions on the realisation of one great idea.

At the same time we cannot help feeling some regret for the indigo planters in the far East, who, after enjoying more than a century of easy prosperity, see now that more serious times are in store for them. They see the day coming when the indigo plantations will disappear, in the same way in which the madder fields of Avignon have vanished. But we are consoled by the knowledge that, especially for India, the time has already come, which has been so vividly described by Sir William Crookes, in one of his addresses to the British Association, as the future in store, sooner or later, for all humanity, the time when bread begins to be scarce. It seems to me that any one who, by bringing about some great commercial revolu-

tion such as we have seen in the indigo trade, causes land in India to become free for the growing of rice and other cereals, renders a great service to large numbers of poor natives, and need therefore not be blamed for lessening to some extent the prosperity of a class of people who have had an unusually good opportunity of accumulating wealth in the past.

It is a strange fact, that with indigo the history of the fight of the madder root against artificial alizarine is almost literally repeated in spite of the great difference of original conditions in the two cases. Madder was a product containing at its best only 4 per cent. of actual colouring matter; the rest was useless fibre and obnoxious impurities which greatly hampered the dyer in his work. Alizarine, entering into competition with this natural product, was, on the contrary, the colouring matter in a pure state, and therefore not only cheaper but also much easier in its application. Indigo, such as we receive it from India and Java, is a manufactured article, the best qualities of which contain 59, 60, or even 70 per cent. of pure dye-stuff, besides impurities which have always been considered as perfectly harmless. Thus the artificial product did not seem to have much scope for improvement as far as the quality came into consideration. Here again we have committed a mistake. We know now that the impurities are not harmless, and that the blues dyed with artificial indigo are quite as superior in brightness and purity of shade to those obtained with natural indigo, as alizarine reds were to madder reds. This has, however, not always proved to be an advantage for the manufacturers of artificial indigo. The world does not ask for bright indigo shades, and a good many prejudices in that respect had to be overcome before artificial indigo was admitted as a legitimate substitute for the natural product in some of its most important applications. Yet a simple consideration will show that it is always easy to deteriorate the brilliancy of a dyed shade, whereas no art of the dyer will suffice to produce brilliant shades on textile fabrics with dye-stuffs that carry their share of dirty admixtures within them.

In its application to the fibre, indigo is perhaps the most remarkable of all dye-stuffs, for it is the principal representative of that extraordinary class of colouring-matters which must be applied by the vat process. This process, which consists in first reducing the dye-stuff into a leuco-compound before applying it to the fibre, on which the original colouring-matter is formed again by the action of the oxygen of the air, seems to have nothing in common with the ordinary dyeing processes. If, however, we consider it more closely, we come to the conclusion that vat colours are a class of dye-stuffs in which the functions of dyeing and of selective absorption of light are distributed on two different forms of the substance, one of which contains two atoms of hydrogen more in its molecule than the other.

This theory is supported to some extent by the fact that what

we are pleased to call leucocompounds, are in the majority of cases by no means colourless. Indigo-white itself is not white but yellow in its alkaline solution which we call a vat. Other vat-dyes have leucocompounds which are even more strongly coloured. Thus the leucocompound of indanthrene, a beautiful new colouring-matter, is blue like indanthrone itself; flavanthrene, a yellow dye-stuff, which has not yet left the laboratory of its inventor, has a blue leucocompound. One may say, that with all vat-colours the real dye-stuff is the leucocompound which is afterwards, when once fixed on the fibre, transformed into a pigment by the oxidising influence of the air.

In 1825 Faraday discovered, in this very house, benzene; the original specimen, prepared by his own hands, is before you. We look upon it reverently, like on a sacred relic bequeathed to us by a master-mind. But what a development has sprung from this first attempt to unravel the mysteries of the aromatic series! Our science as well as our industry have been revolutionised by the investigation of the derivatives of benzene, and the world has been embellished by the gay and brilliant dyes of which it is the mother-substance. The study of the chemistry of these dye-stuffs has become a domain of science which, for variety and fascination, can hardly be surpassed by any other. The deeper we penetrate into it the more it proves an inexhaustible mine of the most subtle scientific thought, yet one which never loses touch with practical life; it is interesting alike to the philosophical mind that wishes to revel in the wonderful perfection and order of nature, and to the philanthropic spirit which rejoices in seeing many thousands of hands occupied and princely fortunes produced by the utilisation of what was only a short time ago a refuse and an encumbrance. It teaches a lesson even to those who are not attached to science and apt to consider it as a kind of pastime for people who lack ability for practical life. For they cannot help seeing that, in this case, the most intricate science has led to something eminently practical, commensurate to a standard which, though unknown to the Bureau International des Poids et Mesures, is to some people the only reliable one, viz. the one of £ s. d.

I am afraid that the high praise which I feel justified in bestowing on what has been the favourite pursuit of my life is not fully substantiated by the contents of this lecture. The subject which I had to treat is so vast, that all I have been able to say is nothing but a sketch or a programme of what would require a long series of lectures if full justice were to be done to it. My one excuse for attempting to sketch, in the short space of one hour, so vast a subject, is the place in which I had the honour to speak: An audience that has been addressed more than once by the pioneers of the chemistry of dye-stuffs, by Faraday, Hofmann, William Perkin, and others, could, from one of the Epigones, not have looked for more, than a few notes and additions.

[O. N. W.]

Friday, May 2, 1902.

SIR WILLIAM CROOKES, F.R.S., Honorary Secretary and  
Vice-President, in the Chair.

A. E. TUTTON, Esq. B.Sc. F.R.S. F.C.S.

*Experimental Researches on the Constitution of Crystals.*

EXPERIMENTAL work in connection with the study of crystals offers attractions of a more than usually fascinating kind. For, in the first place, crystals themselves are such wonderfully beautiful objects; they are, indeed, unquestionably the most beautiful of all the inanimate productions of Nature. It is even doubtful whether we are right in considering them inanimate, for the force of crystallisation, though it may lie dormant for thousands of years, is ever ready, when a suitable environment offers, to re-assert itself. In the second place, the study of crystals involves the investigation of that most exquisite of all the forms of energy, light—that extraordinary effect of wave-motion in the ethereal all-pervading medium, which we now believe to be due to an exceedingly rapid, periodic, oscillating change in the electrical condition of the atoms and molecules of the incandescent light-giving source.

We will allow the beam of light from an electric lantern to fall on this cluster of diamonds, carbon in its most exquisite crystalline form. The diamonds are arranged, as you see, in the shape of a crown, and were generously lent for this lecture by Mr. Streeter. You observe a magnificent play of light waves rippling towards you in every variety of colour and scintillation. The object of the experiment is that you may distinguish the two distinct types of emanation, namely, exterior reflections of white light from the facets and coloured rays due to penetration of the light into the interior structure of the diamonds, and subsequent refraction and reflection outwards again. The former kind you observe best in the innumerable images in white light of the carbon points of the lanterns, reflected on the ceiling and screen.

It is by the determination of the direction of the exterior reflections that we are enabled to ascertain the wonderfully regular angular relations of the various faces of the crystals; and it is by the study of the light which has penetrated that we gain the best information concerning the internal structure.

We shall consider this evening some of the results of a study of the crystals of certain series of definitely related chemical salts.

There has been a great want of correlated work of this kind, having for its definite object the elucidation of the relationship between the chemical composition of a crystallised substance and the peculiar type of symmetry which it exhibits.

The salts which have, up to the present, been studied, are the sulphates and selenates of the alkali metals potassium, rubidium and caesium, which crystallise in the rhombic system of symmetry; and thirty members of the well-known monoclinic series of double sulphates and selenates, containing one of the three alkali-metals just mentioned, another metal of the magnesium or iron type, and six molecules of water of crystallisation.

The research had two main objects. First, to discover the effect of replacing one alkali-metal by another; and second, the effect of replacing the lighter element, sulphur, contained in the acid radicle of the salt, by the heavier element, selenium. The three metals, potassium, rubidium and caesium, belong strictly to the same family of chemical elements, according to the now famous periodic classification of Newlands and Mendeleeff. They are the most electropositive metals known, and the weights of their atoms are related in a most interesting manner, that of rubidium being the mean of the atomic weights of potassium and caesium. It was, therefore, to be expected that any difference of form or properties brought about by the replacement of any one of these metals by another would be as great as could ever be produced by a change of this kind, and it might be hoped would be adequately great to enable a true idea of its character to be obtained. The very fact that no differences in the angles of the crystals of so-called isomorphous salts had, up to the commencement of this work, been detected with certainty, shows how very small, at most, such differences must be. It will also be evident that for such a research only the most perfectly formed and homogeneous of crystals must be employed. It is a primary essential that the faces of the crystals shall yield perfect images of the signal-slit of the goniometer, and in order that this may be so they must be absolutely plane surfaces. Indeed, if one may be forgiven a slight equivocation in the spelling of a word, the ladies present may be interested to hear that the beauty of crystals lies in the planeness of their faces.

The mode of measuring the angles between crystal faces on the goniometer, and at the same time the difficulty offered by imperfect faces, may be illustrated with the aid of this large crystal of quartz. It is mounted upon one of the actual goniometers employed in the work, but the size of the crystal is enormously greater than those actually used in the research, which rarely exceeded the size of a pin's head. Such small crystals are much more free from distortion than larger ones.

You now see on the screen the image of the goniometer signal-slit reflected from one of the faces of the quartz crystal. This image

is an irreproachable one, the face reflecting it being truly plane. Its narrow part is capable of accurate adjustment to a vertical cross-wire. On rotating the crystal so as to bring the image from the next face, of the particular zone which has been previously adjusted, into the field, you observe that this also is a very good image, but much weaker than the other. This is simply because it is derived from a much smaller face, but the face is quite plane. The next image you see is a bad one, being not only a multiple image, but distorted. Such an image would be quite useless for our purpose. Thus, on rotating round the whole zone—for it is one of the geometrical properties of crystals that the faces lie in zones—we find that some images are good and some are bad. In the case of very small crystals it generally happens that the greater number of images afforded by the faces are either one thing or the other, and crystals must be selected yielding the maximum of good images.

The first result of importance that has been brought to light is that, with regard to each series of salts, there is an interesting relationship between the general exterior character—or habit, as the crystallographer terms it—of any triplet of salts containing potassium, rubidium and caesium respectively.

We will see on the screen, for instance, the configurations of the three double salts, potassium zinc sulphate, rubidium zinc sulphate and caesium zinc sulphate. The same planes are present in all, but very differently developed. In the potassium salt the shape is determined by the large development of the prism zone ( $p$  faces), and the large flat end faces of the basal plane,  $c$ . The caesium salt, on the other hand, exhibits a prismatic habit formed by the faces of the clinodome,  $q$ , and the basal plane  $c$  is reduced to a strip. Intermediate between these two types comes the rubidium salt, and this is the case with the rubidium salt of every one of the sixteen triplets examined.

Hence the habit clearly follows the order of the atomic weights of the alkali metals.

The next general result arrived at is, that small angular differences between the faces have been established, but they rarely amount to a degree in magnitude. And what is of even more interest is, that the faces of every rubidium salt are inclined to each other at intermediate angles to those of the potassium and caesium salts.

This important fact may be illustrated by the vacuum-tube model on the table, which has been specially constructed to emphasise the point. The three crystal outlines represent sections through one of the principal planes of the alkaline sulphates or selenates. The outer one represents the outline of caesium sulphate or selenate, the middle one that of the rubidium salt, and the inner one a section of the potassium salt. The intermediate inclination of the domal faces will be clearly apparent. This is only one of some sixty angles which have been examined, and all show the same beautiful progression in the order of the atomic weights.

In the case of the principal angle of the monoclinic series, which determines the inclination of the inclined axis characteristic of that system of symmetry, the change of angle is directly proportional to the change in atomic weight.

Before concluding what may be said about the exterior morphology, reference may be made to one other fact, which follows from that just referred to and from the results of careful determinations of the specific gravity of the salts. The latter enables one to arrive at the molecular volume, which in the case of salts belonging to the same series does actually represent the relative volume of the chemical molecules. The size of the molecules of the rubidium salt was in every case found to be intermediate between the sizes of the molecules of the potassium and cesium salts. By combining these molecular volumes with the lengths of the crystallographical axes as afforded by the angular measurements, it has been possible to determine the relative dimensions, in the three directions of space, of each chemical molecule.

This was preceded by a proof, which has been confirmed by Dr. Fock, of Berlin, from an entirely different point of view, that the unit of the crystal structure in these salts was identical with the chemical molecule, and was not an aggregate of such.

The result has been to show that the sizes, or at any rate the distances apart from centre to centre, of the chemical molecules in the three rectangular directions of space are intermediate in the case of every rubidium salt. Thus the directional dimensions of the molecules, like the angles of the crystal structure, follow the order of the atomic weights of the alkali metals.

This fact is clearly exhibited in exaggerated fashion by the model, and it will be observed that the intermediate position of the rubidium salt is somewhat nearer to that of the potassium salt than to that of the cesium salt.

In turning now to the consideration of the optical characters of the crystals of the series of salts in question, it will be necessary to remember two main facts. The first is, that the symmetry of the rhombic system, in which the sulphates and selenates of the alkalies crystallise, determines that the velocity of light transmission shall be different along the three morphological axes of the crystals, and that two of these directions shall be those of maximum and minimum velocity respectively. In other words, the ellipsoid which, as is well known, in general represents the velocity of light transmitted through a crystalline medium, is one whose three rectangular axes are of unequal lengths, but which is fixed in direction, for these axes are identical in direction with the three morphological axes. The second is, that in the case of the monoclinic double sulphates and selenates the symmetry of the system demands that only one of the three rectangular axes of the optical ellipsoid shall be identical with a morphological axis, the latter being the one symmetry axis of the system. The

ellipsoid may therefore be regarded as free to rotate about this axis, for the inclination of the other two rectangular axes of the ellipsoid, which lie in the plane of symmetry, may be any whatsoever with respect to the two inclined morphological axes which lie in that plane.

Within the three models of sections of our rhombic sulphate crystals you now see three illuminated ellipses. They represent the sections of the three optical ellipsoids; but in this case the inner one corresponds to the cæsium salt, and represents the ellipsoidal line to which light waves emanating from the imaginary centre of the crystal would penetrate in a given interval of time. The middle one shows the distance to which they would penetrate if the crystal were one of rubidium sulphate or selenate; and any point on the outer one, which is much nearer to the middle one than the outer one is, represents the position at which the light waves would arrive in the same interval of time if the crystal were one of potassium sulphate or selenate.

The velocity with which light travels through the crystals of the three salts is thus observed to vary in the same manner as does the atomic weight of the alkali metal present in the salt.

In the case of the monoclinic double sulphates and selenates, we have a further phenomenon of even greater interest exhibited. For not only does the velocity along the three rectangular axes of the ellipsoid vary with the atomic weight, but the possible rotation of the whole ellipsoid about the symmetry axis is found to actually occur; and to occur, moreover, to a very considerable extent, sometimes amounting to as much as  $20^\circ$ .

Further, most interesting of all, the rotation varies in a perfectly regular manner throughout all the triplets, in accordance with the atomic weight of the alkali metal present in the salt. This may be demonstrated to you by means of the lantern slide which you now see projected on the screen. You observe the outline of a crystal, arranged so that the screen represents the symmetry plane, and within it an ellipsoid. The latter is at present arranged as it is usually situated in any potassium salt of the series, its major axis being inclined so that its top is somewhat to the left of the vertical morphological axis. The ellipsoid will now be rotated to the approximate position, further on the left of the vertical axis, which it occupies in any rubidium salt of the series, by means of a simple mechanical device; and again it is rotated much further, to about the situation which it takes up in any cæsium salt.

In this phenomenon the accelerating progression according to the atomic weight of the alkali metal is beautifully exhibited.

It may now interest you to learn how these results have been obtained. We have to determine, first the position of the optical ellipsoid, and next its dimensions. That is to say, we have to determine the velocity of light transmission in all the various direc-



tions in the crystal. Determinations of the refractive index in different directions will afford us the necessary data, and if we can discover the directions of maximum and minimum velocity we shall obtain all that we require if we make the determinations of refractive index for these two directions and for a third direction at right angles to the plane containing them. For these three directions will be those of the three axes of the ellipsoid.

It will next be demonstrated to you how we discover the positions of the axes of the optical ellipsoid.

It is scarcely necessary to introduce to a Royal Institution audience the magnificent pair of Nicol prisms which formerly belonged to the late Mr. Spottiswoode. The analysing Nicol is at present arranged with its vibrating direction parallel to that of the polarising prism, and to the horizontal cross-wire which you see appearing on the screen, so that light passes to the screen.

There is also focussed the outline of a section of a monoclinic crystal, placed between the two Nicols, and which you may take as representing a crystal of one of our double sulphates or selenates; for it behaves precisely similarly, and is immensely larger than any crystal that could be obtained of one of those salts. We now rotate the analyser so that its vibrating direction is at right angles to that of the polariser, when you see the crystal section brilliantly coloured on the dark field.

If, however, we rotate the crystal section in its own plane, you observe that the coloured light becomes weaker, until, at a certain position, it is altogether extinguished. Further rotation causes light to again appear, and if we complete the circle of rotation we shall find that the crystal becomes four times dark and four times light. That is, there are two directions, at right angles to each other, in which extinction occurs. These two directions are those of two axes of the optical ellipsoid. If the crystal is so prepared as to show on its edge traces of one or two natural faces, and if our rotating stage is divided, it is quite easy to determine the angle between any given trace of a face and either of the extinction directions. In the case of monoclinic crystals the section is cut parallel to the symmetry plane, and the reference edge will usually be a trace of one of the faces in the primary zone perpendicular to the symmetry plane. That is the case with the two faces whose traces you see are left after the grinding of the large section you observe on the screen. A much more refined method of measuring the angle between the extinction direction and the basal plane, based on this principle, was employed in the research.

We will next illustrate the determination of the three refractive indices, corresponding to the three velocities along the three axes of the ellipsoid. There is here a large 60°-prism of a crystal which behaves similarly to the salts we are discussing, and which has been specially cut and polished for this lecture by Mr. Hilger. The re-

fracting edge is parallel to an axis of the ellipsoid. Employing it in the usual manner to throw a spectrum on the screen, we observe that instead of a single spectrum, as when we use a prism of glass, we have two spectra produced, differing considerably in their dispersion. Moreover, on placing a Nicol prism in the path of the light, we see that these spectra consist of polarised light, for one extinguishes when the Nicol is arranged with its vibration direction at  $0^\circ$ , and the other when the Nicol is at  $90^\circ$ . One of the spectra, in fact, is formed by light vibrating parallel to the refracting edge, and therefore to that axis of the ellipsoid which runs parallel with it, and the other by light vibrating at right angles to that direction. If, in cutting our prism, we make this perpendicular direction to coincide with a second axis of the ellipsoid, the two spectra, when set to their minimum deviation, will, provided we know also the angle of the prism, at once afford us the data for computing the refractive indices corresponding to the two axes of the ellipsoid in question. A second prism, similarly cut so as to have vibration directions parallel to one of these axes and to the third axis, will afford us the third refractive index as well as a repetition of one of the first two.

You observe that the two spectra are considerably separated on the screen. If the two axial directions are those of maximum and minimum velocity, the amount of separation is a measure of the double refraction. Now it has been observed that the amount of the double refraction also varies progressively according to the atomic weight, and this fact may be illustrated realistically by means of a carefully made lantern slide, reproducing the actual positions, as seen in the spectrometer, of the two spectra afforded by a triplet of salts. The triplet chosen consists of potassium zinc sulphate, rubidium zinc sulphate and caesium zinc sulphate. The spectra are represented by the images of the spectrometer slit for two wavelengths of light, those corresponding to the red and greenish-blue hydrogen lines. The spectra were produced by three prisms of the respective salts, of precisely the same angle, near  $60^\circ$ . You see that the two upper spectra, representing the potassium salt, are the furthest apart, and that the separation diminishes for the rubidium salt, and it becomes so much less in the case of the caesium salt that the two lower spectra formed by this salt partially overlap.

This relative behaviour as regards double refraction is quite general throughout all the four series of salts.

The point can be further illustrated by the curves which you now see projected on the screen. The two outer curves represent the maximum and minimum refraction, and the inner one the intermediate refraction along the third rectangular axis of the ellipsoid. You observe that the two outer curves converge towards each other as the atomic weight of the alkali metal increases.

This leads in four particular cases to perhaps the most interesting

of all the results derived from the work. We will illustrate it by the case of cæsium magnesium selenate. The curves which you now see on the screen are those for the magnesium triplet of double selenates. On arrival at the cæsium salt the convergence has actually brought the curve for the minimum refraction into contact with that for the intermediate refraction, so that we have here a crystal whose total double refraction is exceptionally small, and in which the velocities along two of the three ellipsoidal axes are approximately equal, which is characteristic of tetragonal and hexagonal crystals, but a perfect anomaly in a monoclinic crystal. Let us see, however, if the identity is a fact for all wave-lengths, as would be the case in a truly uniaxial crystal of tetragonal or hexagonal symmetry. We will reproduce for you the appearance in the spectrometer afforded by a prism so cut as to give us the two spectra corresponding to these two intersecting curves, that is, whose vibration directions are those of the two apparently equal axes of the velocity ellipsoid.

The images in three colours which you see are those corresponding to the wave-lengths of red lithium light, green thallium light and violet hydrogen light. You observe that they completely overlap, and if we only used the same magnification as we used for the other images we saw just now, you would say that they are absolutely identical images. We are attempting to faithfully reproduce the whole phenomena by the use of separate slides, shown by two equal lanterns, and when one of them is shut off, the effect is exactly as when a Nicol is introduced at  $0^\circ$  in the spectrometer, which extinguishes one of the spectra. When the other is shut off instead, what you observe is the same as if we rotated the Nicol to  $90^\circ$ , which would extinguish the second spectrum. Commencing with both lanterns on, as when no Nicol is being used, or if it is, it is arranged at  $45^\circ$ , and examining the images closely, we notice that the red and violet images are distinctly double, while the central green image is a truly single one. Now we cut off one lantern, and you please imagine that we are introducing a Nicol at  $0^\circ$ ; the effect has been that the outermost image in the case of both red and violet has disappeared. Now shutting off the other lantern instead, and you please imagine we are rotating the Nicol to  $90^\circ$ , the innermost images disappear. All this time the green image remains fixed and single. This evidently means that for the middle part of the spectrum there is absolute identity of refraction and therefore of velocity, while for the red end there is a minute difference of refraction in one sense, and for the violet end a similar small difference in the opposite sense. The fact is, the two images, corresponding to the two ellipsoidal axes, for red are slightly separated; they approach and coalesce for green; then they pass each other and re-separate on the opposite side of each other as violet is approached.

Thus our crystal is only truly uniaxial for one wave-length of light, and this apparent anomalous refraction is merely the effect of the operation of the rule of progression.

You will have gathered that for the prosecution of this work it has been necessary to prepare some hundreds of  $60^\circ$ -prisms and parallel-sided section-plates, all accurately cut to the desired orientation with respect to the crystal faces. For this purpose it has been found necessary to have the delicate apparatus constructed which you see before you on the table, and a photograph of which is also thrown on the screen. The crystal, held in a grip-holder, is suspended from a refined apparatus which serves not only for the adjustment of a zone of the crystal's faces to the vertical axis of the instrument, as determined by the observer through the telescope of the collimator signal-slit, but also, as the movements are graduated, for its setting to any position with respect to the axis. Separate and interchangeable cutting and grinding gear are provided, and also a delicate means of varying the pressure of the crystal on the grinding disc, so that the most fragile crystals can be manipulated without danger of fracturing them.

It is not too much to say of this instrument, that without it the work described to you this evening would never have been possible.

Another original instrument which you see before you is an apparatus for producing spectrum monochromatic light of any wave-length whatsoever. For all the optical researches have to be carried out in pure monochromatic light, that is, for a series of colours of light, each of which is composed of vibrations of as nearly one wave-length as possible; for all the optical constants vary considerably for different wave-lengths of light. It is essentially a spectroscope constructed to transmit as large a proportion of the light as possible which streams from the condenser of an electric lantern; a broad spectrum is produced by a highly refractive prism, and is focussed on the back of a second slit, which permits only a selected line of the spectrum to escape, in the same manner as in the well-known apparatus of Sir Wm. Abney. By rotation of the prism the spectrum is moved over the exit slit, so as to permit any desired colour to escape, whose wave-length is known from the reading of the calibrated circle on which the prism is mounted.

The apparatus is placed before you just as it is arranged, in front of the goniometer-spectrometer, when determining refractive indices for a series of different wave-lengths.

There will now be introduced to you another means which we possess of determining the position and shape of the ellipsoid. In an ellipsoid having three unequal rectangular axes, it will be evident that if we consider the elliptical section containing the maximum and minimum axes, there must be a point somewhere on each elliptical quadrant where the radius vector will be equal to the intermediate axis. Such are the four points C on the figure projected on the screen. The two sections of the ellipsoid which contain these points and the intermediate axis will consequently be circles, and rays of light which pass through the crystal at right angles to these sections will be able to vibrate with equal velocity in all directions perpen-

dicular to the line of propagation. Consequently in these two directions, which are termed optic axes, the crystal will exhibit no double refraction. When the  $Y$  velocity approaches nearer to the  $X$  velocity the inclination of the two circular sections to each other naturally diminishes, and the angle between the optic axes becomes proportionately less, until at length we have equality of  $X$  and  $Y$ , the ellipsoid becoming a spheroid, with a single optic axis. This is the special case which we observe in tetragonal and hexagonal crystals, such as the well-known cases of calcite and quartz.

We will now see some very beautiful phenomena in connection with these optic axes, employing for the purpose a projection polariscope, which is furnished with a special set of lenses to render the light strongly convergent while passing through the crystal. First let us investigate the phenomena exhibited by one of the uniaxial crystals we have just referred to. A section-plate cut perpendicular to the single optic axis is now between the crossed Nicols, and you see the beautiful spectrum rings and the black cross, characteristic of uniaxial crystals, which are produced.

We will next see the effect produced by a section-plate of a biaxial crystal, similar to the salts we are discussing. The plate is cut perpendicular to that axis of the ellipsoid which is the bisectrix of the acute angle between the optic axes. You observe the loci of the two optic axes are marked by hyperbolic brushes, in the present position of the section, and they are surrounded by separate rainbow-coloured rings, which in turn are surrounded by lemniscates and eventually ellipse-like curves. If we rotate the section  $45^\circ$ , the hyperbolæ join up to form a cross, but the loci of the optic axes remain marked by the rings. These rings are large and brilliant, to render the demonstration clear, and are afforded by a very large section-plate. But for research purposes we require the rings to be very small and the hyperbolæ very narrow, so that the measurement of their position may be very accurate.

We will put in another section-plate, much smaller because of the impossibility of obtaining larger ones, of rubidium magnesium selenate, and you see how small and sharp, although naturally fainter, the rings and hyperbolæ are.

Next let us demonstrate how we measure the angle of separation between the two optic axes. Another section-plate has been arranged on a small goniometer, so that it can be rotated in the plane of the axes. You see we are able to bring first one and then the other optic axis up to the cross wires, which you see also focussed on the screen.

If we note the reading of the goniometer circle while one optic axis is so adjusted, and then rotate until the other is in position and read the circle again, the difference between the two readings will give us the apparent angle between the axes as seen in air.

In order to arrive at the true angle within the crystal, it is necessary to cut another section perpendicular to the bisectrix of the obtuse

angle between the axes, and to measure this obtuse angle. As, however, this large angle is usually invisible in air, owing to internal reflection, it is necessary that both angles shall be measured while the sections are immersed in some highly refractive liquid. A simple calculation, involving the two angles measured, enables us then to deduce the true optic axial angle within the crystal.

The result of a large number of such measurements of optic axial angles has been to show that in all cases where the interference figures are normal, the angle of the rubidium salt is intermediate in value between the angles of separation of the optic axes of the potassium and cesium salts of the same triplet.

We will conclude the lecture by demonstrating to you the beautiful optic axial phenomena in the four abnormal cases to which reference was made when discussing the refraction phenomena, in which for a certain wave-length of light a prism of the crystal only gives one refraction image instead of two.

You see on the screen the type of interference figure which is given by rubidium sulphate. It is characteristic of the few known interesting salts which exhibit the phenomenon of crossed axial plane dispersion.

You see next the interference figure afforded by cesium magnesium selenate. It is characterised by large dispersion, and it will be proved to you in a moment that for blue light this crystal also is apparently uniaxial, and that the figure in white light which you are now contemplating is due to the fact, that for the most luminous colours of the spectrum separation of the optic axes in the horizontal plane occurs.

It would be interesting to analyse this figure by showing you the curves afforded by the crystal in the pure monochromatic light from the spectroscopic illuminator. But although this can be done most brilliantly for one person at a time looking through the so illuminated observing instrument, there is not light enough for projection. But a series of six photographs, for six specific wave-lengths of light, have been taken with the aid of the apparatus, and you now see them on the screen, each with as exact a reproduction of the colour for which it was taken as possible. The first shows the separation for red lithium light, the second the diminished angle for yellow sodium light, the third the still smaller angle for green thallium light, the fourth the further approach towards the centre for greenish-blue hydrogen light, the fifth shows the uniaxial figure in light of wave-length 466 for which crossing occurs, and the sixth shows the separation in the perpendicular plane for violet hydrogen light.

We will also show you another six, to prove to you that not only does change of wave-length in the illuminating light provoke extraordinary changes in the optic axial angle, but that change of temperature is also provocative of remarkable changes of angle. This set represents the phenomena observed at about  $80^{\circ}$ . The angle for

lithium light is now very much smaller than it was at the ordinary temperature; for red hydrogen light it is still smaller, and for sodium light the crossing has now actually arrived, while for thallium green, hydrogen greenish-blue, and the blue light for which crossing occurred at the ordinary temperature, the axes are separated at increasing angles in the perpendicular plane.

Our last experiment will illustrate the effect of change of temperature in the case of caesium selenate. The behaviour of this salt is so similar to that of the long-known case of gypsum, that, as I can obtain a very much larger crystal of this beautiful mineral, suitable for projection purposes, I shall use it to demonstrate the phenomena. You see at the ordinary temperature nothing whatever beyond the fact that some light gets through to the screen. The optic axes are at present separated in the horizontal plane to such an extent that they are well outside the field. We are now warming the crystal, and you see colour making its appearance at the sides; now the axes themselves, surrounded by their coloured rings, are appearing. They approach the centre, they now coalesce to form the uniaxial cross and spectrum circles. They now separate in the vertical plane, and we remove the source of heat, the axes still continuing to separate vertically until the crystal and the metal frame in which it is being heated have taken up the same temperature. Now the motion stops, and the phenomena repeat themselves in the inverse order, once more coming to a cross and circles, and again separating in the horizontal plane, until finally they disappear on the margin of the field.

These beautiful cases of crossed axial plane dispersion, you will remember, are entirely due to the operation of the rule which we found to govern the progress of the double refraction, in accordance with the progress in the atomic weight of the alkali metal, so that these very exceptional cases are in reality strong proofs of the main generalisation derived from this work.

It has thus been amply demonstrated to you that the chief result to which these researches have led is, that the members of every series of salts known to the chemist, which differ by containing different elements of the same family group, exhibit perfectly regular variations in their exterior morphology and in their interior physical properties; and that these variations follow the order of the differences between the atomic weights of those interchangeable elements. Thus, it has been shown that the crystallographical properties of the elements are in line with all their other properties, chemical and physical, in exhibiting the same progressive character which is so conveniently expressed by their atomic weights.

We do not yet know why a particular series of salts chooses the specific type of symmetry which is common to its members, but we have reasonable ground for hope that further work in the direction indicated, together with a successful development of the interesting mathematical and geometrical researches now being conducted by

several fellow-workers, on the possible modes of partitioning space and the types of molecular packing, will eventually lead to a solution of this important question.

During the researches described in this lecture many thousands of crystals have had to be prepared in a state of perfection and purity, many hundreds of section-plates and prisms cut and ground, and innumerable measurements with the most refined of instruments carried out. But one forgets the labour in the contemplation of knowledge truly gained, and one remembers only the delights of the way, the glorious phenomena of colour which one has enjoyed, and the exquisite beauty of the crystals themselves.

[A. E. T.]



Friday, May 30, 1902.

SIR WILLIAM CROOKES, F.R.S., Honorary Secretary and  
Vice-President, in the Chair.

DR. J. A. FLEMING, M.A. F.R.S. *M.R.I.*,  
Professor of Electrical Engineering, University College, London.

*The Electronic Theory of Electricity.\**

CONSIDERABLE progress has been made of late years in our knowledge concerning the structure and relations of atoms and electricity. Recent discoveries have moreover placed in a new light old theories and experimental work. The remarkable investigations and deductions made from his own experiments and those of others, which have led Professor J. J. Thomson to the conclusion that atoms can be split up into, or can give off, smaller masses, which he calls corpuscles, have been explained by him on many occasions.† There seems to be good evidence that in a glass vessel exhausted to a high vacuum, through the walls of which are sealed platinum wires, we have a torrent of small bodies or so-called corpuscles projected from the kathode or negative wire, when the terminals are connected to an induction coil or electrical machine.

Twenty-five years ago Sir William Crookes explored with wonderful skill many of the effects due to electric discharge through such high vacua, and came to the conclusion that they could only be explained by the supposition that there was present in the tube matter in a *fourth state*, neither solid, liquid, nor gaseous, but 'radiant matter' projected in straight lines from the surface of the negative pole or kathode, the particles moving with immense velocity, and all charged with negative electricity. He showed by beautiful experiments that this radiant matter bombarded the glass walls and produced phosphorescence, could be focussed on to metal sheets and render them red hot, and could drive round little windmills or vanes included in the tube. It therefore possesses the quality of inertia,

\* The following pages do not contain a verbatim reproduction of the discourse delivered on this occasion, but are a reprint of an article in the 'Popular Science Monthly,' for May 1902, by the lecturer, covering substantially the same ground, and reproduced here by kind permission of the editor, Professor J. McKeen Cattell.

† See 'Popular Science Monthly,' vol. lix. p. 323, "On Bodies smaller than Atoms," by Professor J. J. Thomson, F.R.S. See also by the same author a paper in the 'Philosophical Magazine' for December 1899, "On the Masses of the Ions in Gases at Low Pressures."

and, in consequence of the electric charge it carries, it is virtually an electric current, and can be deflected by a magnet. The proof which has been given by Professor Thomson that this 'radiant matter' consists of corpuscles, a thousand times smaller than an atom of hydrogen in mass, and that they are shot off from the kathode with a velocity which is comparable with that of light, explains at once both their kinetic energy and also the manner in which they are able to pass through windows of aluminium, as shown by Lenard, and get into the space outside the tube. Furthermore, evidence has been put forward to show that the electric charge carried by each one of these tiny corpuscles is exactly the same as that which a hydrogen atom carries in the act of electrolysis or when it forms a hydrogen ion.

It seems tolerably clear from all the facts of electrolysis that electricity can only pass through a conducting liquid or electrolyte by being carried on atoms or groups of atoms which are called *ions*—i.e. *wanderers*. The quantity thus carried by a hydrogen atom or other monad element, such as sodium, silver or potassium, is a definite natural unit of electricity. The quantity carried by any other atom or group of atoms acting as an ion is always an exact integer multiple of this natural unit. This small indivisible quantity of electricity has been called by Dr. Johnstone Stoney an *electron* or *atom of electricity*. The artificial or conventional unit of electric quantity on the centimetre-gramme-second system, as defined by the British Association Committee on Electrical Units, is as follows:

An *electrostatic unit* of electric quantity is the charge which when placed upon a very small sphere repels another similarly charged sphere, the centres being one centimetre apart, with a mechanical force of one dyne. The *dyne* is a mechanical unit of force, and is that force which acting for one second on a mass of one gramme gives it a velocity of one centimetre per second. Hence, by the law of inverse squares the force in dynes exerted by two equal charges  $Q$  at a distance  $D$  is equal to  $Q^2/D^2$ . Two other units of electric quantity are in use. The *electromagnetic unit*, which is thirty thousand million times as great as the electrostatic unit, and the *practical unit* called the coulomb or ampère-second, which is three thousand million times the electrostatic unit. We can calculate easily the relation between the *electron* and the *coulomb*; that is, between *Nature's unit of electricity* and the British Association unit, as follows:

If we electrolyse any electrolyte, say acidified water which yields up hydrogen at the negative electrode, we find that to evolve one cubic centimetre of hydrogen gas at  $0^\circ \text{C}$ . and 760 mm. we have to pass through the electrolyte a quantity of electricity equal to 8.62 coulombs. For 96,540 coulombs are required to evolve one gramme of hydrogen and 11,200 cubic centimetres at  $0^\circ \text{C}$ . and atmospheric pressure weigh one gramme. The number 8.62 is the quotient of 96,540 by 11,200.

Various arguments, some derived from the kinetic theory of gases,

indicate that the number of molecules of hydrogen in a cubic centimetre is probably best represented by the number twenty million million million  $= 2 \times 10^{19}$ . Hence it follows, since there are two atoms of hydrogen in a molecule, that in electrostatic units the electric charge on a hydrogen atom or hydrogen ion is

$$\begin{aligned} \frac{96540 \times 3 \times 10^9}{11200 \times 4 \times 10^{19}} &= \frac{65}{10^{11}} \text{ of a C.G.S. electrostatic unit} \\ &= \frac{22}{10^{20}} \text{ of a coulomb.} \end{aligned}$$

Accordingly, if the above atomic charge is called *one electron* then the conventional British Association electrostatic unit of electric quantity is equal to 1540 million electrons, and the quantity called a coulomb is nearly five million million million electrons. The electron or the electric charge carried by a hydrogen atom or ion is evidently a very important physical constant. If we electrolyse, that is decompose by electricity aqueous solutions of various salts, such as sodium chloride, zinc chloride, copper sulphate, silver nitrate, we find, in accordance with Faraday's Laws of Electrolysis, that the passage of a given quantity of electricity through these solutions decomposes them in proportionate amounts such that for every 46 grammes of sodium liberated there are 65 of zinc, 63.5 of copper and 216 of silver. These masses are called chemical equivalents. Accordingly, if we imagine a number of vessels placed in a row containing these solutions and by means of platinum connecting links or plates we pass an electric current through the series, for every atom of copper or zinc carried to their respective cathodes, we shall have two atoms of silver or sodium similarly transported. Since the same quantity of electricity must pass through every vessel in the same time, it is evident that the above fact may be interpreted by assuming that whilst an atom of silver or sodium acting as an ion carries one electron, an atom of zinc or copper carries two electrons.

In the same way we may have atoms which carry three, four, five or six electrons. Thus we may interpret the facts of chemical valency and Faraday's Law of Electrolysis in terms of the electron.

We are thus confronted by the idea long ago suggested by Weber and by Von Helmholtz, that the agency we call electricity is *atomic in structure*, that is to say, we can only have it in amounts which are all exact multiples of a certain small unit. Electricity therefore resembles those articles of commerce like cigars, which we can buy in exact numbers, 1, 10, 50, 100, 1000, but we cannot buy half a cigar or five-sixths of a cigar. If then the law which holds good for electricity in association with atoms during electrolysis holds good generally, a very important advance has been made in establishing the fact that there is a small indivisible unit of it which can be multiplied but not divided, and every quantity of electricity, small or large, is an exact integer multiple of this unit, *the electron*.

*Theories of Electricity.*

Various answers have been given at different times to the question—What is electricity? It has been defined as an imponderable fluid, as a force, as a mode of motion, a form of energy, an ether strain or displacement or a molecular motion.

At one time physicists have considered it as a single entity or fluid; at others it has been pronounced to be duplex in nature, and positive and negative fluids or electricities have been hypothecated.

The state of electrification has been looked upon at one period as due to an excess or defect of a single electricity, at others as a consequence of the resolution of some neutral fluid into two components. An electrical charge on a conductor has been regarded as something given to or put upon the conductor, and also as a state of strain or displacement in the surrounding non-conductor. The intelligent but non-scientific inquirer is often disappointed when he finds no simple, and as he thinks essential, answer forthcoming to the above question, and he asks why it cannot be furnished.

We must bear in mind, however, that scientific hypotheses as to the underlying causes of phenomena are subject to the law of evolution and have their birth, maturity and decay. Theory necessarily succeeds theory, and whilst no one hypothesis justified by observations can be looked upon as expressing the whole truth, neither is any likely to be destitute of all degree of truth if it sufficiently reconciles a large number of observed facts.

The notion that we can reach an absolutely exact and ultimate explanation of any group of physical effects is a fallacious idea. We must ever be content with the best attainable sufficient hypothesis that can at any time be framed to include the whole of the observations under our notice. Hence the question—What is electricity?—no more admits of a complete, and final answer to-day than does the question What is Life? Though this idea may seem discouraging, it does not follow that the trend of scientific thought is not in the right direction. We are not simply wandering round and round, chasing some elusive will-o'-the-wisp, in our pursuit after a comprehension of the structure of the universe. Each physical hypothesis serves, as it were, as a lamp to conduct us a certain stage on the journey. It illuminates a limited portion of the path, throwing a light before and behind for some distance, but it has to be discarded and exchanged at intervals because it has become exhausted and its work is done.

The construction and testing of scientific theories is therefore an important part of scientific work. The mere collection of facts or even their utilisation is not the ultimate and highest goal of scientific investigation. The aim of the most philosophic workers has always been to penetrate beneath the surface of phenomena and discover those great underlying fundamental principles on which the fabric of nature rests. From time to time a fresh endeavour has to be made

to reconstruct, in the light of newly acquired knowledge, our scientific theory of any group of effects. Thus, the whole of electrical phenomena have become illuminated of late years by a theory which has been developed concerning the atomic structure of electricity, and this hypothesis is called the Electronic Theory of Electricity.

### *The Atomic Theory.*

The opinion that matter is atomic in structure is one which has grown in strength as chemical and physical knowledge has progressed. From Democritus, who is said to have taught it in Greece, to John Dalton who gave it definiteness, and to Lord Kelvin who furnished the earliest numerical estimate of the size of atoms, in spite of adverse criticism, it has been found to be the best reconciler of very diverse and numerous observed effects. Let us consider what it really means. Suppose we take some familiar substance, such as common table salt, and divide a mass of it into the smallest grains visible to the eye. Each tiny fragment is as much entitled by all tests to be called table salt, or to give it the chemical name, sodic chloride, as a mountain of the material. Imagine that we continue the subdivision under a good microscope; we might finally obtain a little mass of about one hundred-thousandth of an inch in diameter, but beyond this point it would hardly be visible even under a powerful lens. We may, however, suppose the subdivision continued a hundredfold by some more delicate means until we finally arrive at a small mass of about one ten-millionth of an inch in diameter. A variety of arguments furnished by Maxwell, Boltzmann, Loschmidt, Lord Kelvin and others show that there is a high degree of probability that any further subdivision would cause the portions into which the salt is divided to be no longer identical in properties, but there would be two kinds of parts or particles, such that if all of one kind were collected together they would form a metal called sodium, and if all of the other kind were similarly picked out they would form a non-metal called chlorine. Each of these smallest portions of table salt, which if divided are no longer salt, is called a *molecule* of sodic chloride, and each of the parts into which the molecule is divisible is called an *atom*, of sodium or of chlorine. In dealing with the dimensions of these very small portions of matter an inch or a centimetre is too clumsy a unit. To express the size of an atom in fractions of an inch is worse than stating the diameter of an apple in fractions of a mile. Every one knows what is meant by a millimetre; it is nearly one twenty-fifth part of an inch. A metre is equal to a thousand millimetres. Suppose a millimetre divided into a thousand parts. Each of these is called a *micron* and denoted by the Greek letter  $\mu$ . This however is still too large a unit of length for measuring the size of atoms, so we again divide the micron into a thousand parts and call each a micromillimetre or *micromil*, and denote it by the symbol  $\mu\mu$ . Lord Kelvin's estimate of the diameter of a molecule is that it lies

between one hundredth of a micromil and two micromils, that is between  $0.01 \mu\mu$  and  $2 \mu\mu$ . This is certainly a very wide estimate, but it is the best yet to hand, and for present purposes we may take it that an atom is a small portion of matter of approximately one millionth of a millimetre or one micromil ( $1 \mu\mu$ ) in diameter. On the same scale the wave-length of a ray of yellow light is about  $0.6 \mu$  or  $600 \mu\mu$  that is six hundred times the size of an atom. We know nothing as yet about the relative sizes of different kinds of atoms. In the next place, as regards the number of molecules in a given space, various distinguished physicists, Maxwell, Kelvin, Boltzmann, Van der Waals and others, have given estimates for the number of molecules in a cubic centimetre of air at ordinary temperature and pressure, which vary between  $10^{18}$  and  $10^{21}$ , between a million billion and a thousand million billion. All we can do is to take a rough mean of these different values, and we shall consider that in one cubic centimetre of hydrogen or other gas at  $0^\circ \text{C}$ . and 760 mm. or freezing point and ordinary pressure there are about  $2 \times 10^{19}$  or twenty million million molecules. To understand what this enormous number means we must realise that if we could pick out all the molecules in one cubic inch of air and place them side by side in a row, small as they are individually, the row would extend nearly twice the distance from the earth to the sun.

Having provided ourselves with a rough idea of the sizes and numbers of the molecules of any gas, we proceed to obtain an idea of their weight or mass. Since 11,162 cubic centimetres of hydrogen gas at  $0^\circ \text{C}$ . and 760 mm. weigh one gramme, it follows from the above facts that each molecule of hydrogen has a mass of nearly  $1/10^{23}$  of a gramme. To weigh these tiny atoms we must therefore take a unit of weight equal to one-billionth of one-billionth of a gramme and then on this scale the hydrogen molecule weighs 10 such units. We may obtain in another way an illustration of the mass, size and number of the molecules of any gas in the following manner:

First as to size. We can, in a good Whitworth measuring instrument, detect a variation in length of a metal bar equal to one millionth of an inch. This short length would be occupied by 25 molecules placed in a row close together. We can in a good microscope see a small object whose diameter is one hundred-thousandth of an inch. In a small box of this size we could pack 16 million molecules close together. The smallest weight which can be weighed on a very good chemical balance is one hundredth of a milligramme. The united weight of one million million million molecules of hydrogen would therefore just be detectable on such a balance.

#### *Ultra-Atomic Matter.*

Until a few years ago our knowledge of the divisibility of matter may be said to have ended with the chemical unit, the atom. But of late years information has been steadily accumulating which has

made us acquainted with matter in a finer state of subdivision. For a long time a controversy was carried on, whether the radiation in a high vacuum tube which proceeds from the kathode was a material substance or a wave motion of some kind. But no fact yet found is inconsistent with the notion which originated with Sir William Crookes that the transfer which takes place is that of something which has the inertia quality of matter, and his term "radiant matter" is a peculiarly suitable phrase to describe the phenomena. The great advance which has since been made, by Professor J. J. Thomson and others, is that of measuring accurately the amount of bending which a stream of this radiant matter experiences under a known magnetic force, and from this deducing the ratio between the mass of the radiant particle and the electric charge carried by it. This measurement shows that if the radiant matter consists of corpuscles or particles, each of them carries a charge of one electron, but has a mass of about one-thousandth of a hydrogen atom.

The evidence therefore exists that Crookes' "radiant matter" (also called the "kathode rays") and Thomson's "corpuscles," are one and the same thing, and that these corpuscles may be described as fragments broken off from chemical atoms and possessing only a small fraction of their mass. These particles are shot off from the negative terminal or kathode of the vacuum tube with a velocity which is from one-fifth to one-third the velocity of light.

Moreover, it has been shown that when the kathode rays pass through a thin metal window in a vacuum tube and get into the space outside, thus forming Lenard's rays, they are likewise only the same or similar corpuscles in the space outside rather than inside the vacuum tube. Finally it has been proved that these electrified corpuscles are present as well in the mass of a gas through which Röntgen rays have passed, also in the mysterious radiation called Becquerel rays which proceeds from uranium and other radio-active substances, also in all flames, near all very hot bodies and in the air near certain metallic surfaces, on which ultra-violet light falls. In every case the corpuscle is charged with an electron charge of negative electricity. If a corpuscle originates as a fragment chipped off from an electrically neutral atom and is negatively charged, it follows that the remainder of the atom of matter is left positively charged.

The word "atom" therefore, as far as it signifies something which *cannot be cut*, is becoming a misnomer as applied to the chemical unit of matter, because this latter is capable of being divided into two parts of very unequal size. First, a small part which is negatively electrified and which is identically the same, no matter from what chemical atom it originates, and secondly, a much larger mass which is the remainder of the atom and is positively electrified, but which has a different nature depending on the kind of chemical atom broken up. The question has then begun to be debated whether we can distinguish between the corpuscle and the electric charge it carries,

and if so in what way. In other words, can we have an unelectrified corpuscle, or is the corpuscle so identified with its electric charge that they are one and the same thing? It has been shown experimentally that an electric charge in motion is in effect an electric current, and we know that an electric current possesses something equivalent to inertia, that is, it cannot be started and stopped instantly, and it possesses energy. We call this electric inertia *inductance*, hence the question arises whether the energy of the corpuscles when in motion is solely due to the electric inductance or whether it is partly due to what may be called the ponderable inertia of the corpuscle.

This very difficult question has not yet been even approximately settled. At the present moment we have no evidence that we can separate the electron charge from the corpuscle itself. If this is the case, then the corpuscles taken together constitute for all practical purposes negative electricity, and we can no more have anything which can be called electricity apart from corpuscles than we can have momentum apart from moving matter. For this reason it is sometimes usual to speak of the corpuscle carrying its charge of one electron of negative electricity simply as *an electron*, and to drop all distinction between the electric charge and the vehicle in or on which it is conveyed.

It is remarkable that so far no one has been able to produce or find a corpuscle positively electrified. Positive electricity is only known in association with masses as large as atoms, but negative electricity is united with corpuscles or masses only a small fraction of the size of an atom. This does not prove that an atom may not include positive corpuscles or electrons, but only that so far we have not been able to isolate them.

### *The Electronic Theory of Electricity.*

From this point of view a theory of electricity originates called the electronic theory. The principal objects of consideration in this theory are these electrons which constitute what we call electricity. An atom of matter in its neutral condition has been assumed to consist of an outer shell or envelope of negative electrons associated with some core or matrix which has an opposite electrical quality, such that if an electron is withdrawn from the atom the latter is left positively electrified.

A neutral atom *minus* an electron constitutes the natural unit of positive electricity, and the electron and the neutral atom *minus* an electron are sometimes called negative and positive ions. Deferring for a moment a further analysis of possible atomic structure we may say that with the above hypothesis in hand we have then to express our statements of electrical facts in terms of the electron as the fundamental idea.

All that can be attempted here is a very brief exposition of the



success which has so far attended this effort to create a new range of electrical conceptions. Let us consider first the fundamental difference between substances in respect of electrical conductivity. In the electronic theory, what is the distinction between conductors and non-conductors? It must be remembered that on the electronic hypothesis an electric current is a movement of electrons. Hence a conductor must be a substance in which electrons free to move exist. It is considered therefore that in metals and good conductors a certain proportion of the atoms are broken up into positive and negative ions or into electrons and remainders of atoms which we may call coelectrons. There may be a constant decomposition and recombination of atoms taking place, and any given electron so to speak flits about, now forming part of one atom and now of another and anon enjoying a free existence. It resembles a person visiting from house to house forming a unit in different households and in between being a solitary person in the street. In non-conductors, on the other hand, the electrons are much restricted in their movements, and can be displaced a little way but are pulled back again when released. The positive and negative ions or electrons and coelectrons never have the opportunity to part company very far.

The reader who is familiar with the modern doctrine of the ionization of salts in solution will see that a close similarity exists between this view of the atomic state of a metal and the chemical state of a salt in solution. The ionic theory of solution is that if some salt, say sodic chloride, is placed in water a certain proportion of the molecules of sodic chloride are dissociated into sodium and chlorine ions, that is to say, atoms possessing electric charges, and the electric conductivity of the solution is due to the mobility of these saline ions.

On the electronic theory a certain proportion of the atoms of a conductor are similarly in a state of electronization. The application of an electromotive-force to the conductor thus at once causes the electrons to begin to migrate. If we compare conductors and non-conductors we shall see that the former are mostly elementary bodies, the metals and alloys or graphitic carbon, whilst the latter are all very complex substances such as glass, ebonite, the oils, shellac, gutta-percha, etc. These last have large and complex molecules, but the good conductors have all simple molecules and small atomic volumes. The exceptions apparently are sulphur and carbon in the form of diamond. When, however, we remember that carbon and sulphur are elements very prone to polymerise and so to speak combine with themselves they may not really be an exception. The electrons may, therefore have much more difficulty in exchanging from atom to atom or in making their way between or through the molecules when these are very complex than when they are simple.

The question then may be asked why these free electrons do not all escape from the conductor. The answer is that there must be an equal quantity of electrons and coelectrons or remainders of atoms

or of so-called negative and positive ions and the strong attraction between these involves the expenditure of work to separate them. The radio-active substances, such as uranium, polonium, radium, actinium and others, to which so much attention has been paid lately, do seem to have the power of emitting their corpuscles or electrons and scattering them abroad, and hence can only do this at the expense of some of their own internal molecular energy or else drawing upon the heat of surrounding bodies.

We come next to the explanation of the familiar fact of electrification by friction. Why is it that when we rub a glass rod with a bit of silk the two things are equally and oppositely electrified? To explain this on the electronic theory we have to consider the state of affairs at the surface of any substance immersed say in air. At the surface where the air and glass meet there will be an electronization of atoms which appears to result in the formation of a double layer of electrons and coelectrons or negative and positive ions. This is probably an attempt on the part of the glass and air to combine chemically together. The same state exists at the surface of the silk. When we rub these two things together these double layers are very roughly treated and are broken up. The whole lot of electrons and coelectrons or residual portions of atoms get mixed up and more or less divided up between the two surfaces. As however every negative electron has its positive coelectron, it follows that what one surface gains the other must lose. Hence in the end we may have a majority of negative ions or electrons left on the one surface and a majority of positive ions or coelectrons left on the other surface; and the glass and the silk are then electrified with equal quantities but opposite signs. Owing to the mutual repulsion of the similar electrons the charge resides wholly on the surface.

This conception of the existence of a double layer of opposite electricities or ions at the surface of contact of two substances has been put forward to account for the familiar effect of the electrification of air by falling drops of water. It has long been known that the air in the neighbourhood of waterfalls of fresh water is electrified negatively, whereas the air in the neighbourhood of splashing salt water, as at the seaside, is positively electrified, and the explanation that has been given by Professor J. J. Thomson is that this is due to the breaking up of this double layer of ions at the surface of the drop when it strikes the ground.

#### *Atomic Valency.*

At this stage it may be well to indicate that any valid theory of electricity must involve an explanation of the facts of chemical combination and chemical valency as well. At present all ideas on the structure of atoms must necessarily be purely speculative. So much advance has been made however in the development of a department of chemistry called stereo-chemistry that we need not despair of coming to know in time much about the architecture of atoms and molecules.

The way is cleared, however, for some consistent explanations if we can assume that one or more free electrons can attach themselves to a neutral atom and so give it a negative charge of electricity. We may suppose as a first assumption that in a neutral atom which is otherwise complete, there exist localities at which one or more electrons can find a permanent attachment. The atom is then no longer neutral but negatively electrified. If the atom can as it were accommodate *one* electron it is a monovalent element, if *two* it is divalent, and so on. If it cannot accommodate any at all it is an *avalent* or *non-valent* element.

Consider the case of gaseous molecules. Chemical facts teach us that the molecules of free gaseous hydrogen, oxygen or other gases contain two atoms, so that these free molecules are represented by the symbols  $H_2$ ,  $O_2$ , etc. In these cases hydrogen and oxygen are so to speak combined with themselves. We can explain this by the supposition that most neutral atoms are unstable structures. In contact with each other some lose one or more electrons and an equal number gain one or more electrons. Hence in a mass say of hydrogen we have some atoms which are positively electrified and some which are negatively electrified then called atomic ions, and these ions united pair and pair form the molecules of hydrogen which may be represented by  $(H^+, H^-)$ . Similarly for other gases. Certain neutral atoms such as those of argon are monatomic and non-valent and these appear to be unable to enter into combination either with each other or with other atoms. Accordingly, in a mass of free hydrogen there are no free electrons and all the positively charged and negatively charged H atoms are in union. Hence the gas is a non-conductor of electricity. But we can make it a conductor by heating it to a high temperature. The explanation of this is that a high temperature dissociates some of the molecules into atoms and these under the action of electric force move in opposite directions, thus creating an electric current. Thus air at ordinary temperatures is an almost perfect non-conductor, but at a white heat it conducts electricity freely.

The monovalent elements like hydrogen are those neutral atomic structures which can lose one electron or take up one electron, becoming respectively positive atomic ions and negative atomic ions. In the same way the divalent elements such as oxygen are those neutral atomic structures which can part with two electrons and take up two, and so on for trivalent, quadrivalent, etc., atoms. The work required to remove the second electron probably is very much greater than that required to remove the first. Hence in polyvalent atoms the valencies have unequal energy values.

Consider now a mass of intermingled oxygen and hydrogen consisting of neutral molecules. The state is a stable one as long as all the molecules are neutral. If, however, we dissociate a few of the hydrogen and oxygen molecules by an electric spark or by heat then there is a recombination. A positive oxygen ion unites with two negative hydrogen ions and a negative oxygen ion with two positive

hydrogen ions and the result is two neutral molecules of water. This combination takes place because the union of oxygen ions with hydrogen ions to form water evolves more heat and exhausts more potential energy than the combination of oxygen with oxygen and hydrogen with hydrogen ions in equivalent quantity. The energy set free by the union of the O and H is sufficient to continue the dissociation of further gaseous molecules, so the action is explosive and is propagated throughout the mass.

There is however a broad distinction between the elements in this respect, viz.: that some atoms are prevalently electropositive and others electronegative. A metallic atom for instance is electropositive, but the atoms of non-metals are mostly electronegative. Moreover metals in the mass are electrically good conductors, whereas non-metals in the mass are non-conductors or bad conductors. This may be explained by the varying degree of force required to detach electrons from neutral atoms and conversely the varying degree of attachment of electrons for neutral atoms. Thus we may consider that the metallic atoms lose very easily one or more electrons, and also that there is a somewhat feeble attachment in their case between the neutral atom and the free electron. Hence metals in the mass are conductors because there are plenty of free electrons present in them. On the other hand, in the case of non-metallic atoms the force required to detach one or more electrons from the atom is much greater, and conversely the attachment of free electrons for the neutral atom is larger. Accordingly, in non-metals there are few free electrons, and they are therefore non-conductors. Moreover, the presence of positive and negative atomic ions causes them to link together into more or less complex molecules, and they exhibit polyvalency and act as the grouping elements in molecular complexes. This is a very characteristic quality of the elements sulphur, silicon and carbon.

Helmholtz long ago laid stress on the fact that certain physical and chemical effects could only be explained by assuming a varying attraction of electricity for matter. The same idea followed out leads to an hypothesis of chemical combination and dissociation of salts in solution. Thus a molecule of sodic chloride is the electrical union of a monovalent sodium ion or sodium atom *minus* one electron with a chlorine ion which is a chlorine atom *plus* one electron. It may be asked why in this case does not the extra electron pass over from the chlorine to the sodium ion and leave two neutral atoms. The answer is because the union between the electron and the chlorine is probably far more intimate than that between the atomic groups. These latter may revolve round their common centre of mass like a double star, but the electron which gives rise to the binding attraction may be more intimately attached to the atomic group into which it has penetrated.

*Voltaic Action.*

Any theory of electricity must in addition present some adequate account of such fundamental facts as voltaic action and magneto-electric induction. Let us briefly consider the former. Suppose a strip of copper attached to one of zinc and the compound bar immersed in water to which a little hydrochloric acid has been added.

All chemical knowledge seems to point to the necessity and indeed validity of the assumption that the *work* required to be done to remove an electron from a neutral atom varies with the atom. Conversely the attraction which exists between a free electron and an atom deprived of an electron also varies. Accordingly the attraction between atomic ions, that is, atoms one of which has gained and one of which has lost electrons, is different. Upon this specific attraction of an atomic ion for electrons or their relative desire to form themselves into neutral molecules depends what used to be called chemical affinity. Mr. Rutherford has shown that negative ions gave up their charges more readily to some metals than others, and most readily to the electro-positive metals. Hence a zinc atomic ion is more ready to take up electrons and again become neutral than a copper ion.

Consider then the simple voltaic couple above described. In the electrolyte we have hydrogen ions which are H atoms *minus* an electron, and chlorine ions which are chlorine atoms *plus* an electron. These are wandering about in a menstruum which consists of water molecules and hydrochloric acid molecules. Then in the metal bar we have zinc and copper divalent ions which are these atoms each *minus* two electrons, and also an equivalent number of free and mobile electrons.

If we adopt Volta's original view of contact electricity, we must assume that at the surface of contact of the metals there is some action which drives electrons across the boundary from the zinc to the copper. This may be due to the neutral copper atom having a slightly greater attraction for electrons than the neutral zinc atom. The zinc is therefore slightly electrified positively and the copper negatively. Accordingly in the electrolyte the negative chlorine ions move to the zinc and combine with positive zinc ions, forming neutral zinc chloride, two chlorine ions going to one zinc ion. The hydrogen ions therefore diffuse to the copper side and each takes up a free electron from the copper, becoming neutral hydrogen atoms and there escape.

In proportion as the zinc atomic ions are removed from the zinc bar and the corresponding free electrons from the copper, so must there be a gradual diffusion of electrons from the zinc bar to the copper bar across the metallic junction. But this constitutes the voltaic current flowing in the circuit. It is a current of negative electricity flowing from zinc to copper and equivalent to a positive current from copper to zinc. The energy of this current arises from the differential attraction of zinc and copper ions for chlorine ions, and is therefore

the equivalent of the exhaustion of the chemical potential energy of the cell. Thus the electronic theory outlines for us in a simple manner the meaning of voltaic action. Even if we do not admit the existence of a metallic junction volta contact force, the theory of the cell may be based on the view that the movement of the saline ions in the electrolyte is determined by the law that that motion takes place which results in the greatest exhaustion of potential energy. Hence the chlorine ions move to the zinc and not to the copper.

In the same manner the electronic theory supplies a clue to the explanation of the production of an electric current when a conductor is moved across a magnetic field. Every electron in motion creates a magnetic force. Hence a uniform magnetic field may be considered as if due to a moving sheet of electrons. The 'cutting' of a conductor across a magnetic field will therefore be accompanied by the same reactions as if a procession of electrons were suddenly started in it. This, however, would involve at the moment of starting a backward push on surrounding electrons, just as when a boat is set in motion by oars the boat is pushed forward and the water is pushed back. Hence there is an induced current at the moment when the field begins in the conductor. Similarly the reaction at stopping the procession would drag the surrounding electron with it. Accordingly the induced current when the field ceases is in the opposite direction to that when it begins.

The electronic theory has in the hands of other theorists such as Professors P. Drude and E. Riecke been known to be capable of rendering an account of most thermomagnetic effects on metals, contact electricity, the so-called Thomson effects in thermoelectricity, and also the Hall effect in metals when placed in a magnetic field.

### *Electrons and Æther.*

The ultimate nature of an electron and its relation to the æther has engaged the attention of many physicists, but we may refer here more particularly to the views of Dr. J. Larmor whose investigations in this difficult subject are described in his book on 'Æther and Matter' and also in a series of important papers in the 'Transactions' of the Royal Society of London, entitled 'A Dynamical Theory of the Electric and Luminiferous Medium.'\* Larmor starts with the assumption of an æther which is a frictionless fluid, but possesses the property of inertia; in other words, he assumes that its various parts can have motion with respect to each other and that this motion involves the association of energy with the medium. He regards the electron as a strain centre in the æther, that is as a locality from which æther strain radiates. Electrons can therefore be either posi-

\* Phil. Trans. Roy. Soc., 1893, 1895, 1898.

tive or negative according to the direction of the strain, and to every positive electron there is a corresponding negative one. Atoms according to him are collocations of electrons in stable orbital motion like star clusters or systems.

An electron in motion is in fact a shifting centre of æther strain and it can be displaced through a stationary æther just as a kink or knot in a rope can be changed from place to place on the rope.

An electron in vibration creates an æther wave, but it radiates only when its velocity is being accelerated and not when it is uniform.

The type of æther which Larmor assumes as the basis of his reasoning is one which has a rotational elasticity, that is to say, the various portions of it do not resist being sheared or slid over each other, but they resist being given a rotation round any axis. Starting from these postulates and guided by the general and fundamental principle of Least Action, he has erected a consistent scheme of molecular physics in which he finds an explanation of most observed facts.

The discovery by Zeeman of the effects of a strong magnetic field in triplicating or multiplying the lines in the spectrum of a flame placed in a magnetic field meets with an obvious explanation when we remember that the effect of a magnetic field on an electron in motion is to accelerate it always transversely to its own motion and the direction of the field. Hence it follows that a magnetic field properly situated will increase the velocity of an electron rotating in one direction and retard it if rotating in another. But a linear vibration may be resolved into the sum of two oppositely directed circular motions and accordingly a magnetic force properly applied must act on a single spectral line, which results from the vibration of an electron in such manner as to create two other lines on either side, one representing a slightly quicker and the other a slightly slower vibration.

The notion of an electron or point charge of electricity as the ultimate element in the structure of matter having been accepted, we are started on a further inquiry as to the nature of the electron itself. It is obvious that if the electron is a strain centre or singular point in the æther, then corresponding to every negative electron there must be a positive one. In other words, electrons must exist in pairs of such kind that their simultaneous presence at one point would result in the annihilation of both of them.

On the view that material atoms are built up of electrons we have to seek for a structural form of atom which shall be stable and equal to the production of effects we find to exist.

The first idea which occurs is that an atom may be a collection of electrons in static equilibrium. But it can be shown that if the electrons simply attract and repel each other at all distances according to the law of the inverse square no such structure can exist. The next idea is that the equilibrium may be dynamic rather than static, that an atom may consist of electrons, as suggested by Larmor, in orbital

motion round each other, in fact that each atom is a miniature solar system.

Against this view, however, Mr. T. H. Jeans\* has pointed out that an infinite number of vibrations of the electrons would be possible about each state of steady motion and hence the spectrum of a gas would be a continuous one and not a bright-line spectrum.

If we are to assume an atom to consist wholly of positive and negative electrons or point charges of electricity, Mr. Jeans has suggested that we may obtain a stable structure by postulating that the electrons, no matter whether similar or dissimilar, all repel each other at very small distances.

We might then imagine an atom to be built up of concentric shells of electrons like the coats of an onion alternately positive and negative, the outermost layer being in all cases negative. The difference between the total number of positive and negative electrons is the valency of the atom.

On this view an atom of hydrogen would consist of from 700 to 1000 positive and negative electrons arranged in concentric layers in a spherical form. The vibrations which emit light are not those of the atom as a whole but of the individual electrons which compose it.

The reason for assuming that in all cases the outermost layer of electrons is negative is that if it were not so, if some atoms had their outer layers of negative and some of positive electrons, two atoms when they collided would become entangled and totally lose their individuality. There would be no permanence. Hence our present atoms may be, so to speak, the survivors in a struggle for existence which has resulted in the survival only of all atoms which are of like sign in the outer layer of electrons. We see an instance of a similar action in the case of the like directed rotation of all the planets round the sun which is due to the operation of the law of conservation of angular momentum. As a consequence of the equality of sign of the outer layer of electrons two atoms cannot approach infinitely near to each other. They mutually repel at very small distances. This suggestion affords a possible clue to the reason why we only know at present free negative electrons; it is because we can only detach a corpuscle or electron from the outer layer of an atom. It is clear, however, that the complete law of mutual action of electrons has yet to be determined. We have also to account for gravitation, and this involves the postulate that all atomic groups of electrons without regard to sign must attract each other. Hence we need some second Newton who shall formulate for us the true law of action of these electrons which form the "foundation stones of the material universe." Facts seem to suggest that the complete mathematical expression for the law of mutual action of two electrons must show:

1. That at exceedingly small distances they must all repel each other without regard to sign.

\* 'Mechanism of Radiation,' Proc. Phys. Soc. Lond., vol. xvii. p. 760.



2. That at greater distances positive electrons must repel positive and negative repel negative, but unlike electrons attract, with a force which varies inversely as the square of the distance.

3. Superimposed on the above there must be a resultant effect such that all atoms attract each at distances great compared with their size without regard to the relative number of positive and negative electrons which compose them, inversely as the square of the distance.

In this last condition we have the necessary postulate to account for universal gravitation in accordance with Newton's law.

It is conceivable, however, that this differential or resultant universal attraction to which gravitation is due, is only true of electrons when gathered together so as to form atoms. In other words, every atom attracts every other atom; but every electron does not attract every other electron. Universal gravitation may be an effect due to the collocation of electrons to form atoms and molecules, but not an attribute of electrons in themselves, though, if the gravitative effect is proportional to the product of the total number of electrons in each mass, the Newtonian law will be fulfilled. It has been also suggested that a sufficient source for the necessary resultant mass attraction may be found in a slight superiority of the attractive force between two opposite electrons over the repulsion between two similar electrons.

### *Conclusion.*

In the above sketch of the electronic theory we have made no attempt to present a detailed account of discoveries in their historical order or connect them especially with their authors. The only object has been to show the evolution of the idea that electricity is atomic in structure, and thus these atoms of electricity called electrons attach themselves to material atoms and are separable from them. These detachable particles constitute as far as we yet know negative electricity. The regular free movements of electrons create what we call an electric current in a conductor, whilst their vibrations when attached to atoms are the cause of æther waves or radiation, whether actinic, luminous, or thermal. The æther can only move and be moved by electrons. Hence it is the electron which has a grip of the æther and which, by its rapid motions, creates radiation, and in turn is affected by it. We have therefore to think of an atom as a sort of planet accompanied by smaller satellites which are the electrons. Moreover the electrons are capable of an independent existence, in which case they are particles of so-called negative electricity. The atom having its proper quota of electrons is electrically neutral, but with electrons subtracted, it is a positive atomic ion, and with electrons added to it it is a negative atomic ion. It has been shown from a quantitative study of such diverse phenomena as the Zeeman effect, the conductivity produced in gases by Röntgen rays

or by ultra-violet light and from the magnetic deflection of kathode rays, that in all cases where we have to deal with free moving, or vibrating electrons, the electric charge they carry is the same as that conveyed by a hydrogen atom in electrolysis.

There is good ground for the view that when a gas is made incandescent, either by an electric discharge or in any other way, the vibrating bodies which give rise to the light waves are these electrons in association with the atom. The energy of mass movement of the atom determines temperature, but the fact that we may have light given out without heat, in short, *cold light*, becomes at once possible if it is the vibrating electric particle attached to the atom which is the cause of eye-affecting radiation or light.

Lorentz, Helmholtz, Thomson and others have shown that such a conception of atomic structure enables us to explain many electro-optic phenomena which are inexplicable on any other theory. Maxwell's theory that electric and magnetic effects are due to strains and stresses in the æther, rendered an intelligible account of electric phenomena, so to say, in empty space, and its verification by Hertz placed on a firm basis the theory that the agencies we call electric and magnetic force are affections of the æther. But the complications introduced by the presence of matter in the electric and magnetic fields presented immense difficulties which Maxwell's theory was not able to overcome.

The electronic theory of electricity, which is an expansion of an idea originally due to Weber, does not invalidate the ideas which lie at the base of Maxwell's theory, but it supplements them by a new conception, viz., that of the electron or electric particle as the thing which is moved by electric force and which in turn gives rise to magnetic force as it moves. The conception of the electron as a point or small region towards which lines of strain in the æther converge, necessitates the correlative motion of positive and negative electrons. We are then led to ask whether the atom is not merely a collocation of electrons. If so, all mechanical and material effects must be translated into the language of electricity. We ought not to seek to create mechanical explanations of electrical phenomena but rather electrical ones of mechanical effects. The inertia of matter is simply due to the inductance of the electron, and ultimately to the time element which is involved in the creation of æther strain in a new place. All the facts of electricity and magnetism are capable of being re-stated in terms of the electron idea. All chemical changes are due to the electric forces brought into existence between atoms which have gained or lost electrons. If moving electrons constitute an electric current, then electrons in rotation are the cause of magnetic effects. In optics it is capable of giving a consistent explanation of dispersion, absorption and anomalous dispersion and the relation of the index of refraction to the dielectric constant. A scientific hypothesis, with this wide embrace, which opens many closed doors and enables us to trace out the hidden connection

between such various departments of physical phenomena, is one which must continue to attract investigators. Physical inquirers are at present, however, groping for guiding facts in this difficult field of investigation, but we have confidence that mathematical and experimental research will in due time bring the reward of greater light.

[J. A. F.]

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# PHYSICAL SCIENCES

The discourses of the Royal Institution are unique in character. Each Friday between October and June, a well-known authority is invited to give a general review of his subject, and he is asked not to assume any expert scientific knowledge on the part of his listeners. A tradition has grown up around the "Royal Institution Discourse" which is regarded as a special occasion calling for a talk distinguished by simplicity and clarity and, when appropriate, illustrated by interesting experiments and demonstrations. Most of the discourses are on scientific subjects, but the arts are also represented.

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